PB84-226067

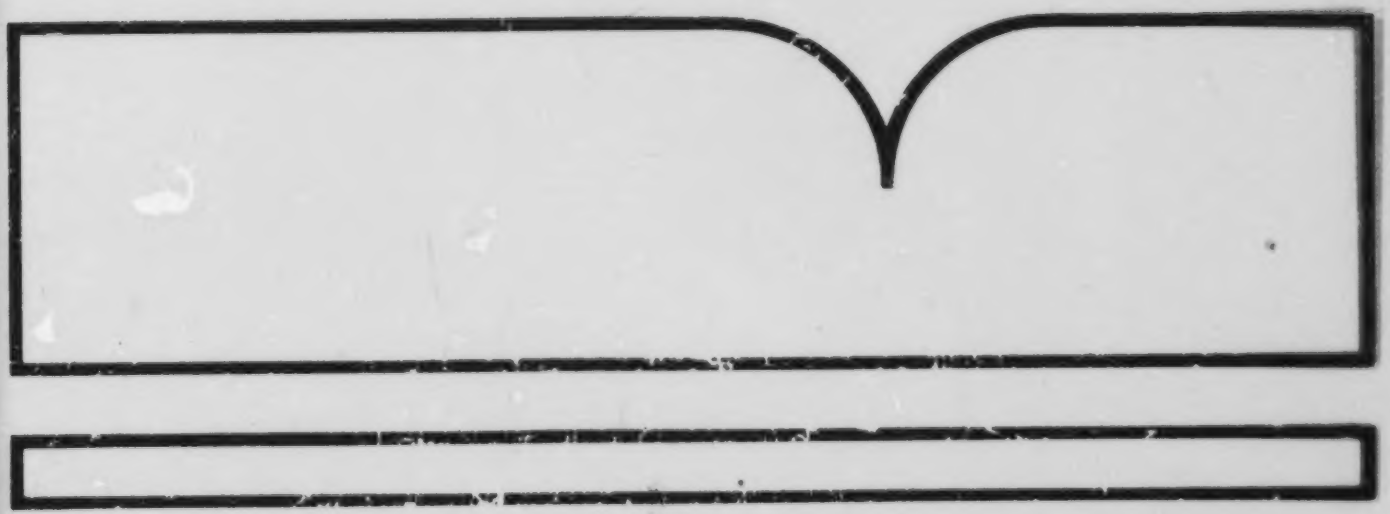
Technical Discussions Relating to the Use of Carbon Bond Mechanism in OZIPM/EKMA (Ozone Isopleth Plotting with Optional Mechanism Empirical Kinetic Modeling Approach)

Systems Applications, Inc., San Rafael, CA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

May 84



U.S. Department of Commerce
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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-450/4-84-009		PB84 226067

4. TITLE AND SUBTITLE	5. REPORT DATE
Technical Discussions Relating to the Use of Carbon Bond Mechanism in OZIPM1/EKMA	May 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J. P. Killus and G. Z. Whitten	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Systems Applications, Inc. 101 Lucas Valley Road San Rafael, California 94903	11. CONTRACT/GRANT NO. Contract 68-02-3570
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency Office of Air Quality Planning and Standards MDAD, AMTB, Mail Drop 14 Research Triangle Park, North Carolina 27711	Final 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

U.S. EPA Contact: Gerald L. Gipson

16. ABSTRACT

The document discusses the use of the Carbon Bond 3 (CB-3) mechanism with the city-specific Empirical Kinetics Modeling Approach (EKMA). Topics addressed include: (1) a description of the CB-3 mechanism, (2) background information of the formulation of key mechanism parameters, and (3) discussions on the treatment of initial conditions, emissions, background ozone, and background precursors with EKMA/CB-3.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
ozone control strategies photochemical pollutants models SIPs carbon bond mechanism	EKMA OZIPP	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
unlimited		92
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB84-226067

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-84-009
May 1984

Air

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Technical Discussions Relating To The Use Of The Carbon Bond Mechanism In OZIPM/EKMA

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NATIONAL TECHNICAL
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SPRINGFIELD, VA. 22161

EPA-450/4-84-009

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Monitoring And Data Analysis Division
Office Of Air Quality Planning And Standards

U.S. Environmental Protection Agency
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park

May 1984

10

This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication as received from the contractor. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, neither does mention of trade names or commercial products constitute endorsement or recommendation for use.

EPA-450/4-84-009

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SECTION 1

INTRODUCTION

This document is intended to fulfill several purposes:

(1) Recommend the specific form of the Carbon-Bond Mechanism (CBM-III/EKMA) to be used with the Empirical Kinetic Modeling Approach (EKMA) to estimate the impact of reducing emissions of volatile organic compounds (VOC) and/or oxides of nitrogen (NO_x) in reducing peak ozone values downwind or within a city;

(2) Examine the reactive organic composition of urban air in order to describe its photochemical behavior and to recommend specific values for CBM-III/EKMA parameters needed to simulate the reactivity of the urban composition;

(3) Apply information and experience obtained in past-modeling applications of the CBM-II to indicate how available emissions, air quality and meteorological data are used in the modeling procedure necessary for EKMA applications; and

(4) Provide one means for Air Pollution Control Agencies to check the completeness and suitability of analyses performed with the model to support the need for urban VOC emission controls.

The Empirical Kinetic Modeling Approach (EKMA) is a procedure for using an ozone isopleth diagram to estimate the impact of controlling urban volatile organic compound (VOC) and/or NO_x emissions on peak hourly ozone concentrations. Both ambient 0600-to-0900 NMOC/NO_x ratios measured in the urban core and peak hourly ozone measured within or downwind of the city are needed to apply an isopleth diagram in the EKMA procedure. Other information requirements, supplied either by measurements or prior assumptions, depend on the nature of the atmospheric model and the kinetic mechanism employed.

The atmospheric model described in this guidelines document is the city-specific EKMA. The city-specific EKMA modeling procedure has also been referred to as "Level III analysis." These two terms are synonymous. The conventional, city-specific EKMA consists of two components: The OZIPP model and the EKMA procedure (i.e., OZIPP/EKMA) (EPA 1978 a, b; Whitten and Hogo, 1978). OZIPP (Ozone Isopleth Plotting

Package) is a computer program that allows the user to plot maximum hourly ozone concentrations as an explicit function of initial (0800) ambient concentrations of nonmethane organic compounds (NMOC) and NO_x within the urban area (EPAc). The OZIPP computer program uses the Dodge photochemical mechanism. Another program--OZIPM (Ozone Isopleth Plotting with Optional Mechanisms)--may use any kinetic mechanism; this program is used in conjunction with the CBM-III/EKMA.

The conventional EKMA (OZIPP/EKMA) relies on an empirical analysis of the reactivity of automobile exhaust as described by a surrogate photochemical mechanism (Dodge/EKMA). In the validation procedure underlying OZIPP/EKMA, a series of smog chamber experiments using automobile exhaust were simulated using a kinetic mechanism for a mixture of propene and butane. The power of this technique lies in its use of empirical calibration data to adjust the simulation model. The calibration procedure will tend to compensate for many uncertainties or inadequacies in the photochemical mechanism. Key weaknesses in the approach are (1) the assumption that all urban hydrocarbon emissions are equivalent to auto exhaust, and (2) the inability of the mechanism to adjust for changes in the state of knowledge of photochemistry without extensive recalibration and revalidation.

The Carbon-Bond Mechanism (CBM) attempts to address these deficiencies. The CBM has been validated with the Bureau of Mines auto exhaust data, which was used to validate the Dodge/EKMA mechanism (Jeffries, Salmi, and Sexton, 1981).* The validation set for the CBM-III/EKMA also includes multicomponent smog chamber experiments across a broad range of hydrocarbon speciation and outdoor smog chamber experiments using natural sunlight. To our knowledge, the Carbon-Bond Mechanism is the most extensively validated and applied kinetic mechanism that currently exists.

Because of the wide range of applications that have used the Carbon-Bond Mechanism, it is possible to draw on a considerable body of knowledge for use in atmospheric simulations involving the CBM. Also, because the CBM-III/EKMA is a condensation of the explicit chemistries of known

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* The version of the Carbon-Bond Mechanism used in the study of Jeffries, Salmi, and Sexton (1981) was the CBM-II, the immediate precursor of the CBM-III, which this document describes. The CBM-II is also used in the Systems Applications Airshed Model, which has been used in many of the atmospheric studies from which information in this document is derived. However, the CBM-III is very similar in structure and performance to the CBM-II (differing primarily in the technical description of aromatic oxidation), and information used to support the CBM-II may also be used for the CBM-III/EKMA.

compounds, it is usually possible to relate specific parameters and rate constants in the mechanism to precise photochemical phenomena. Many of the relevant parameters in the CBM-III/EKMA, therefore, are not either empirical, "adjustable" or "tuning" parameters, but instead are calculated directly from the hydrocarbon speciation in the urban mix.

This document is divided into six sections: Section 2, examines hydrocarbon speciation in urban areas; Section 3 calculates rate constants and parameters that depend on the hydrocarbon mix; Section 4 presents the same calculations for photolysis rates; Section 5 describes ambient data and emission inputs into OZIPM; and Section 6, recommends the background or "clean air" values for ozone, NO_x, and hydrocarbons to be used in atmospheric simulations. With the information supplied in this document, it should be possible to use the OZIPM model to prepare a set of city-specific isopleths, which can then be used in an EKMA analysis.

SECTION 2

USING THE CARBON-BOND MECHANISM

In its current form, the Carbon-Bond Mechanism (CBM-III/EKMA) treats the reactions of six types of carbon atoms: (1) single-bonded carbon atoms, whose principal constituent is paraffinic carbon molecules (PAR), (2) relatively reactive double-bonded carbon (OLE), (3) slow double bonds, which are almost exclusively ethylene (ETH), (4) reactive aromatic rings (ARO), (5) carbonyl compounds such as aldehydes and ketones (CARB), and (6) highly photolytic α-dicarbonyl compounds such as methyl glyoxal and biacetyl (DCRB). Some other types of carbon atoms can also be treated within this set. For instance, highly reactive internal double-bonded carbon atoms were shown by Whitten, Killus, and Hogo (1980) to be equivalent to two carbonyls per double bond. Hence three levels of olefin reactivity can be treated in the CBM (slow as in ETH, relatively reactive terminal olefins as in OLE, and highly reactive internal olefins as in 2 CARB per bond). Appendix B lists the CBM fractions recommended for a variety of organics.

The use of the molecular bond rather than the whole molecule as the principal unit may at first seem confusing to those whose experience is solely with molecular reactions. However, several major advantages associated with the bond-group-reaction principle make the conceptual effort involved worthwhile. The primary advantage is that the Carbon-Bond Mechanism does not require the sometimes uncertain calculation of "average molecular weight." The carbon number of each carbon-bond group is fixed (Table 1):

TABLE 1. CARBON NUMBERS OF CARBON-BOND GROUPS

Carbon-Bond Group	Carbon Number (carbon atoms per molecule)
PAR	1
ETH	2
OLE	2
ARO	6
CARB	1 (plus 1 oxygen atom)
DCRB	3 (plus 2 oxygen atoms)

In a lumped molecular mechanism, chemical reactions might be expected to alter the average molecular weight of each species category. When this phenomenon occurs, it is impossible to perform mass-balance calculations on the reactive organic compounds remaining in the model simulation. The Carbon-Bond Mechanism allows precise hydrocarbon mass-balance calculations to be made, thus facilitating the estimation of the importance of phenomena like long-range smog precursor transport and day-to-day carry-over of pollutants. Moreover, whereas most lumped molecular mechanisms do not conserve carbon, the Carbon-Bond Mechanism conserves carbon and follows each hydrocarbon fraction to its end products (generally CO or CO_2, but occasionally aerosol or nonreactive hydrocarbons).

Although the Carbon-Bond Mechanism has been designed to minimize the problems of rate constant averaging and specification of lumped parameters, any highly condensed mechanism must contain some parametric approximations. The problem of rate constant averaging is somewhat reduced in the CBM-III/EKMA because the range of reactivities of carbon bonds is generally smaller than the range of reactivities for molecules. The parameters that do exist in the CBM-III/EKMA may be related to specific features of the hydrocarbon mix. Moreover, in the design of the mechanism, there was an attempt to minimize the sensitivity to the parameters.

In the following three sections we discuss three important issues regarding use of the CBM-III/EKMA. (1) hydrocarbon speciation, (2) specification of parameters, and (3) specification of photolysis rates. We first treat the issue of hydrocarbon speciation using realistic examples of urban hydrocarbon mixes, in order to use these real cases for the specification of parameters.

SPECIATION OF EMISSIONS AND ATMOSPHERIC CONCENTRATIONS INTO BOND CATEGORIES: THE TOTAL CARBON PRINCIPLE

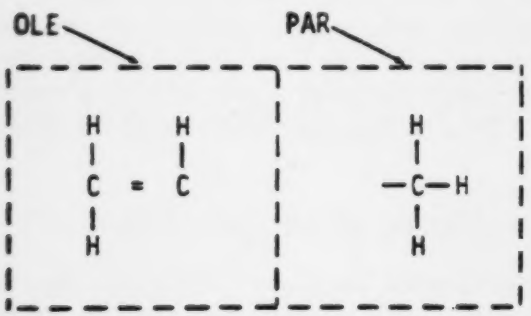
Several important principles must be considered in the application of the Carbon-Bond Mechanism. First, all carbon must be accounted for. Thus, if one adds all of the carbon in each bond category of emissions, the sum should equal the total carbon emitted. Although this principle appears simple and obvious, there are practical complications. Emissions of solvents, for example, are usually given in kilograms of emissions, but methyl alcohol (CH_2OH) is a solvent in which most of the weight is represented by the oxygen atom in the methanol molecule. Another example is the case of automobile exhaust emissions, which are usually reported in gm/mi. of hydrocarbon <u>as methane</u>--i.e., each carbon atom measured is assumed to have a molecular weight of 16 gm/mole. Evaporative emissions, on the other hand, are reported as straight mass, which means that a lower molecular weight is called for. Accounting for all carbon is further complicated by the fact that the procedures used to obtain automobile

exhaust hydrocarbon estimates do not respond efficiently to all reactive species. Aldehydes, for example, are not often measured by standard procedures and must be added to the exhaust emissions estimates.

THE VOLUMETRIC EQUIVALENCE PRINCIPLE

The second important principle to remember when using the Carbon-Bond Mechanism is that the volumetric concentrations (in ppm) of most species used with the CBM are similar to both the volumetric measurements and the molar concentrations used in other mechanisms. One ppm of aromatic hydrocarbon bonds in the CBM is usually equivalent to 1 ppm of aromatic hydrocarbons in a lumped mechanism.*

The major exception to the equivalence of speciation between the CBM and molecular mechanisms is the PAR species, which includes not only the carbon in paraffinic molecules, but also single-bonded carbon in other molecules. A molecule of propylene, for example, contains one single-bonded carbon in addition to the olefinic bond:



In other words, the CBM total reactive hydrocarbon (RHC) given in ppmC must equal

$$(OLE \times 2) + (ETH \times 2) + (ARO \times 6) + CARB + (DCRB \times 3) + PAR = RHC \text{ (in ppmC)} \quad .$$

---

* This is not true, however, for "surrogate mechanisms" in which all hydrocarbons are assumed to be represented by some mixture of surrogate hydrocarbons (e.g., propylene and butane). Comparison of speciation in the CBM with that in such a surrogate mechanism is obviously impossible.

SURROGATE COMPOUNDS (CARBONYLS)

A minor exception to the rule of equivalent speciation lies in the relationship of CARB as a reaction product to other species. Some compounds, especially internal olefins (e.g., trans-2-butene), react much more rapidly than do terminal olefins such as propylene. Thus, instead of creating a new species with an atmospheric lifetime of only a few minutes, we chose to treat internal olefins as if they had already reacted (i.e., as if an internal olefinic bond were already transformed to two carbonyls).

In a prior report (Killus and Whitten, 1982), we suggested that a surrogate carbonyl be added when a cycloalkane is treated. This suggestion was based on the conjecture that cycloalkanes were more reactive than normal alkanes, due to breakage in the ring structure subsequent to reaction with OH. More recent analysis of smog chamber data for cycloalkanes indicates that though they may be somewhat more reactive than n-alkanes, the difference is insufficient to justify the addition of a surrogate carbonyl. Thus, cycloalkanes should be treated as PAR in the CBM-III/EKMA. The effect of this change on overall speciation is slight, since cycloalkanes account for less than 2 percent of the total reactive carbon in typical urban mixes, and the surrogate carbonyl from this source is less than 6 percent of total carbonyl (less than 1 percent overall reactive organics, ROG). This change has been noted in the speciation tables in Appendix B.

EXAMPLES OF HYDROCARBON SPECIATION IN THE CBM-III/EKMA

In this section we perform three example calculations necessary to separate reactive organics in urban hydrocarbon samples into the appropriate carbon bond species. The three examples are for Los Angeles over a 10 year period; the changes in hydrocarbon speciation over this period is an indication of the effect of the increased use of unleaded gasoline. As we will see, this change resulted in a fairly substantial increase in the aromatics fraction.

Example 1

Example 1 calculates the carbon-bond concentrations that would be used for the ambient hydrocarbon measurements reported by Kopczynski et al. (1972). Gas chromatographic analysis (GCA) accounted for 90 percent of total nonmethane hydrocarbons as identified by flame ionization detection (FID). Table 2a gives the carbon fraction allocated to each bond category for each molecular species as calculated from the bond-splitting information given in Appendix B. The calculated molar concentration for each bond group is also given. Table 2b gives the sum of each bond category as well as the carbon fraction for each bond category for

Example 1

TABLE 2. CARBON-BOND CONCENTRATIONS APPLIED TO AMBIENT HYDROCARBON MEASUREMENTS (Kopczynski et al., 1972).

(a) Carbon-Bond Concentrations in ppb

Measured Hydrocarbon Olefins		Carbon Fraction							Molar Concentrations					
		ppbC	ETH	OLE	ARO	PAR	CARB	NR	ETH	OLE	ARO	PAR	CARB	NR
Ethylene		151	1.0						75.5					
Propylene		60		0.67		0.33				20.0		20.0		
1-Butene	(16)	47*		0.5		0.5				11.75		23.5		
Isobutene	(31)													
trans-2-Butene	(12)	12*				0.5	0.5					6.0	6.0	
Methylacetylene	(-)													
cis-2-Butene		8				0.5	0.5					4.0	4.0	
1,3-Butadiene		11		1.0						5.5				
1-Pentene		11		0.4		0.6				2.2		6.6		
2-Methyl-1-butene		15		0.4		0.6				3.0		9.0		
trans-2-Pentene		22				0.6	0.4					13.2	8.8	
cis-2-Pentene		10				0.6	0.4					6.0	4.0	
2-Methyl-2-butene		29				0.6	0.4					17.4	11.6	
1-Hexene		15		0.33		0.67				2.5		10.0		
Unknown 7†		9		0.33		0.67				1.5		6.0		
Unknown 8†														
Subtotal		400							75.5	46.4		121.7	34.4	

Continued

TABLE 2. Continued.

Measured Hydrocarbon		Carbon Fraction							Molar Concentrations					
Aromatics		ppbC	ETH	OLE	ARO	PAR	CARB	NR	ETH	OLE	ARO	PAR	CARB	NR
Toluene		271			0.86	0.14					38.7	38.7		
Ethylbenzene		67			0.75	0.25					8.4	16.8		
p-Xylene		100			0.75	0.25					12.5	25.0		
m-Xylene		215			0.75	0.25					26.9	53.8		
o-Xylene		87			0.75	0.25					10.9	21.8		
n-Propylbenzene		21			0.67	0.33					2.3	7.0		
m-Ethyltoluene (37)		111			0.67	0.33					12.3	37.0		
p-Ethyltoluene														
tert-Butylbenzene (0)		23			0.60	0.40					2.3	9.2		
o-Ethyltoluene														
sec-Butylbenzene	(47)	137*			0.60	0.40					13.7	54.8		
1,2,4-Trimethylbenzene	(90)													
1,3,5-Trimethylbenzene		29			0.67	0.33					3.2	9.7		
Isopropylbenzene		76			0.67	0.33					8.4	25.3		
Subtotal		1137									139.6	299.1		

Continued

TABLE 2. Continued.

Measured Hydrocarbon Paraffins	ppbC	Carbon Fraction ETH	OLE	ARO	PAR	CARB	NR	Molar Concentrations ETH	OLE	ARO	PAR	CARB	NR
Ethane	191				0.2		0.8				38.2		152.8
Propane	140				0.5		0.5				70.0		70.0
Isobutane	65				1.0						65.0		
n-Butane	286				1.0						286.0		
Isopentane	312				1.0						312.0		
n-Pentane	171				1.0						171.0		
Cyclopentane (22) 2-Methylpentane (116)	138*				1.0						138.0		
3-Methylpentane	68				1.0						68.0		
n-Hexane	82				1.0						82.0		
2,4-Dimethylpentane	89				1.0						89.0		
Cyclohexane	16				1.0						16.0		
3-Methylhexane	68				1.0						68.0		
n-Heptane	40				1.0						40.0		
Methylcyclohexane	49				1.0						49.0		
Unknown 1	6				1.0						6.0		
Unknown 2	11				1.0						11.0		
Unknown 3	37				1.0						37.0		
Unknown 4	28				1.0						28.0		
Unknown 5	23				1.0						23.0		
Unknown 6	80				1.0						80.0		
(Acetylene)	160				0.5		0.5				80.0		80.0
Subtotal	2060										1757.2		302.8

* Concentration in parenthesis are estimates of concentrations (ppbc) of compounds with similar chromatographic retention times.

† Assume molecular weight of 6 carbons and 12 hydrogens.

Continued

TABLE 2. Concluded.

(b) Carbon-Bond Speciation Category*

Species	Σ Molar Concentrations (ppb)	Carbon Fraction
ETH	75.5	0.042
OLE	46.4	0.026
ARO	139.6	0.233
PAR	2178.0	0.606
CARB	34.4	0.010
Non-Methane Nonreactive	302.8	0.084

* Gas chromatograph accounted for 3597 ppbC (3294 ppbC RHC + 303 ppbC nonreactive). Flame ionization analysis (FIA): TNMHC = 4.0 ppmC (4000 ppb). Carbon fractions based on 3597 ppbC.

the measured hydrocarbon mix. This information could be directly input to OZIPM, a computer program designed to generate EKMA-type isopleth diagrams using any kinetic mechanism.

Kopczynski et al. (1972) do not report carbonyl data for aldehydes or ketones. The response of aldehydes and ketones to FID and GCA is inefficient. The carbon fraction shown for the CARB species in Table 2b consists exclusively of surrogate carbonyls--compounds such as internal olefins (which form carbonyls rapidly); precise carbonyl data are lacking. As discussed later in this chapter, the additional carbonyls must be estimated.

Example 2

Example 2 (Table 3) also represents ambient sampling in the Los Angeles area (Calvert, 1976). In this case, however, the measurements are reported in molar units. To calculate CBM units from molar units, the appropriate bonds-per-molecule factor (from Appendix B) is multiplied by the molar concentration.

Calvert (1976) stated that roughly 85 percent of total carbon atoms were detected as individual species. Thus about 0.35 ppmC remain unaccounted for in the analysis. It is probable that a substantial fraction of these unmeasured hydrocarbons consist of aromatic compounds. This is evident from the absence of compounds such as trimethyl benzene and ethyl toluene, which were observed in the study described in Example 1, and which are known to occur in gasoline (Mayrsohn et al. 1975). The unmeasured compounds are likely to be those with a high molecular weight and low concentration--another indication that aromatics are the principal constituent. Thus, the aromatic fraction noted in Table 3 is probably a lower bound.

Example 3

Example 3 (Table 4) consists of data obtained for Los Angeles in 1981 and reported by Grosjean et al. (1981). The reported concentrations in $\mu g/m^3$ have been converted into ppbC and then split into carbon-bond concentrations as in Example 1. Overall hydrocarbon recovery in this data was very high, over 96 percent. The most noteworthy feature of the 1981 hydrocarbon data is the high proportion of aromatic hydrocarbons. As noted previously, this is probably due to the increased use of unleaded gasoline in the period 1975-1980.

The data of Grosjean et al. also contained measurements of carbonyl compounds, although these were measured separately, since carbonyls are difficult to measure with gas chromatographs, and flame ionization detectors (FIDs) have a low response to aldehydes and ketones. Carbonyls

Example 2

TABLE 3. LOS ANGELES AMBIENT MEASUREMENTS. (Source: Calvert, 1976).

(a) Reported in Molar Units

Compound	[RH],ppm Molar Basis	Bonds per Molecule x Concentration					
		NR	OLE	ETH	PAR	ARO	CARB
CH_4	2.01						
C_2H_6	0.049	0.078			0.0196		
C_2H_4	0.043			0.043			
C_2H_2	0.038	0.038			0.038		
C_3H_8	0.037	0.0555			0.0555		
C_3H_6	0.0087		0.0087		0.0087		
iso-C_4H_{10}	0.012				0.048		
n-C_4H_{10}	0.037				0.148		
1-C_4H_8	0.0015		0.0015		0.0030		
iso-C_4H_8	0.0030				0.009		0.003
iso-C_5H_{12}	0.0443				0.2215		
n-C_5H_{12}	0.0162				0.0810		
Cyclo-C_5H_{10}	0.0026				0.013		
1-C_5H_{10}	0.004		0.004		0.012		
2-Methylbutene	0.0008				0.0024		0.0016
2,3-Dimethylbutane*	0.0008				0.0048		
2-Methylpentane	0.0110				0.066		
3-Methylpentane	0.0100				0.06		
1-Hexene	0.0017		0.0017		0.0068		
n-Hexane	0.0100				0.06		
Cyclohexane**	0.0107				0.0642		
2,2,3-Trimethylbutane	0.0077				0.0539		
C_6H_6	0.0082	0.041			0.0082		
2-Methylhexane	0.0069				0.0483		
3-Methylhexane	0.0063				0.0441		

Continued

* Incorrectly reported as 2,2 dimethylbutene by Calvert (1976).

** Incorrectly reported as cyclohexene by Calvert (1976).

TABLE 3. Concluded.

Compound	[RH], ppm Molar Basis	Bonds per Molecule x Concentration					
		NR	OLE	ETH	PAR	ARO	CARB
1-Heptene	0.0044		0.0044		0.022		
$n\text{-}C_7H_{16}$	0.0043				0.0301		
Methylcyclohexane	0.0037				0.0259		
2,2,3- and 2,3,3-Trimethylpentane	0.0019				0.0152		
2,2,4-Trimethylpentane	0.0025				0.02		
Toluene	0.020				0.02	0.02	
1-Methylcyclohexene	0.0047				0.0235		0.0094
2,2,5-Trimethylhexane	0.0010				0.009		
$n\text{-}C_8H_{18}$	0.0021				0.0168		
EtC_6H_5	0.0041				0.0082	0.0041	
p,m-Xylenes	0.014				0.028	0.014	
o-Xylene	0.0060				0.012	0.006	
$n\text{-}C_9H_{20}$	0.0013				0.0117		
$n\text{-}PrC_6H_5$	0.0010				0.003	0.001	
$sec\text{-}BuC_6H_5$	0.0050				0.02	0.005	
$n\text{-}C_{10}H_{22}$	0.0011				0.011		
$n\text{-}C_{11}H_{24}$	0.0010				0.011		
$n\text{-}C_{12}H_{26}$	0.0003				0.0036		
CO	1.91						
Total		0.2125	0.0203	0.043	1.367	0.0501	0.014

(b) Carbon Bond Splits for Identified Compounds

Compound	NMHC (ppm)	ppmC	Carbon Fraction of NMHC
NR	0.2125	0.2125	0.105
OLE	0.0203	0.0406	0.020
ETH	0.043	0.086	0.043
PAR	1.367	1.367	0.0676
ARO	0.0501	0.301	0.149
CARB	0.014	0.014	.007
Total Identified ROG:		2.021	

TABLE 4. EXAMPLE OF LIGHT AND HEAVIER MOLECULAR-WEIGHT HYDROCARBON COMPOSITION IN AMBIENT LOS ANGELES AIR. (Source: Grosjean et al., 1981).

Hydrocarbon	Amount ($\mu g/m^3$)	Molar Concentration in CB Units (ppb)						
		ppbC	NR	OLE	ETH	PAR	ARO	CARB
Ethane	13.5	18.9	15.1			3.8		
Ethylene	21.8	30.52			15.26			
Acetylene	11.1	15.54	7.77			7.77		
Propane	17.3	24.22	12.11			12.11		
Propene	10.3	14.42		4.81		4.81		
Propyne	-	-						
Propadiene	-	-						
Isobutane	24.2	33.88				33.88		
Butane	53.2	74.48				74.48		
1-butene	2.2	3.08		0.77		1.54		
Isobutene	6.6	9.24				6.93		2.31
trans-2-butene	5.9	8.26				4.13		4.13
cis-2-butene	-	-						
Isopentane	48.4	67.76				67.76		
Pentane	32.1	44.94				44.94		
3-methyl-1-butene	1.8	2.52		0.504		1.51		
1,3-butadiene	-	-		-		-		
1-pentene	0.9	1.26		0.252		0.756		
Isoprene	-	-						
trans-2-pentene	-	-						
cis-2-pentene	-	-						
2-methyl-2-butene	-	-						
2,2-dimethylbutane	-	-						
Cyclopentene	-	-						
Cyclopentane	3.0	4.2				4.2		
2,3-dimethylbutane	3.9	5.46				5.46		
2-methylpentane	14.1	19.74				19.74		
cis-4-methyl-2-pentene	-	-				-		
3-methylpentane	11.9	16.66				16.66		
2-methyl-1-pentene	4.2	5.88		0.98		3.92		

Continued

TABLE 4. Continued.

Hydrocarbon	Amount ($\mu g/m^3$)	Molar Concentration in CB Units (ppb)						
		ppbC	NR	OLE	ETH	PAR	ARO	CARB
Hexane	9.3	13.02				13.02		
trans-2-hexene	-	-						
2-methyl-2-pentene	-	-						
cis-2-hexene	-	-						
Methylcyclopentane	10.6	14.84				14.84		
2,2,3-trimethylbutane	-	-						
2,4-dimethylpentane	2.7	3.78				3.78		
1-methylcyclopentene	-	-						
Benzene	10.4	14.56	12.1			2.43		
Cyclohexane	4.6	6.44				6.44		
2-methylhexane	4.7	6.58				6.58		
2,3-dimethylpentane	7.3	10.22				10.22		
3-methylhexane	7.3	10.22				10.22		
Dimethylcyclopentanes	5.0	7.0				7.0		
2,2,4-trimethylpentane	5.6	7.84				7.84		
Heptane	5.0	7.0				7.0		
Methylcyclohexane	5.4	7.56				7.56		
Ethylcyclopentane	-							
2,5-dimethylhexane	-							
2,4-dimethylhexane	3.1	4.34				4.34		
2,3,4-trimethylpentane	2.0	2.8				2.8		
Toluene	138.7	194.18				27.74	27.74	
2,3-dimethylhexane	0.9	1.26				1.26		
2-methylheptane	4.8	6.72				6.72		
3-methylheptane	2.7	3.78				3.78		
2,2,5-trimethylhexane	-	-						
Dimethylcyclohexane	-	-						
Octane	2.7	3.78				3.78		
Ethylcyclohexane	1.0	1.4				1.4		
Ethylbenzene	24.9	34.86				8.72	4.36	
p- and m-xylene	109.1*	152.74				38.18	19.09	
Styrene	1.7	3.19				0.40	0.40	0.40

Continued

TABLE 4. Concluded.

Hydrocarbon	Amount ($\mu g/m^3$)	Molar Concentration in CB Units (ppb)						
		ppbC	NR	OLE	ETH	PAR	ARO	CARB
o-xylene	28.3	39.62				9.9	4.95	
Nonane	1.7	2.38				2.38		
Isopropylbenzene	-	-						
Propylbenzene	3.7	5.18				1.73	0.58	
p-ethyltoluene	5.8	8.12				2.7	0.90	
m-ethyltoluene	2.4	3.36				1.12	0.37	
1,3,5-trimethylbenzene	2.7	3.78				1.26	0.42	
o-ethyltoluene	3.1	4.34				1.45	0.48	
tert-butylbenzene	-	-				-		
1,2,4-trimethylbenzene	9.9	13.86				4.62	1.54	
secbutylbenzene	2.2	3.08				1.23	0.31	
1,2,3-trimethylbenzene	1.8	2.52				0.84	0.28	
Decane	1.6	2.24				2.24		
Methylstyrene ***	0.8	1.49		0.083		0.165	0.165	0.165
1,3-diethylbenzene	2.7	3.78				1.51	0.378	
1,4-diethylbenzene	2.6	3.64				1.456	0.364	
1,2-diethylbenzene	-							
Undecane	-							
Dodecane	-							
α-pinene	-							
β-pinene	-							
Limonene	-							
Myrcene	-							
Total		1016.46	47.08	7.40	15.26	543.0	62.33	7.0
Carbon Fraction			0.05	0.015	0.03	0.53	0.368	0.01 (+0.034 measured carbonyls; see text)

* Assumed split: p-xylene - 36 ppb; m-xylene 73 ppb

** 27.1 $\mu gm/m^3$ unidentified compounds
identified compounds > 0.96 total NMHC.

*** Assumed split: 50% A-methylstyrene, 50% B-methylstyrene

reported by Grosjean et al. were C_1 to C_4 aldehydes plus acetone and benzaldehyde. Data indicate a 22.4 ppb formaldehyde concentration and 35.83 ppb of total carbonyls. This amounts to a 0.034 fraction of measured carbonyls which should be added to the 0.01 measured surrogate carbonyl fraction in Table 4. This addition will cause a summnation of carbon fractions slightly greater than 1.0 because carbonyls are not measured by GC or FID instruments. It should also be noted that Grosjean (1982) reported a variety of unidentified carbonyl compounds in Los Angeles measurements. The 0.044 carbon fraction noted in Table 3 is therefore a lower limit.

Carbonyl Compounds

In the first two examples presented in this section, only surrogate carbonyls could be included in the speciations because carbonyl compounds per se (aldehydes and ketones) could not be detected by the instrumentation that was used. Yet carbonyl compounds were undeniably present and they are significant contributors to smog chemistry. Therefore, some estimates of carbonyl emissions must be made.

In addition to their role in the radical initiation of the smog process, a significant fraction of hydrocarbon reactivity results from the oxidation of carbonyl compounds by the hydroxyl radical.* Kopczynski, Kuntz, and Bufalini (1975) compared the reactivity of an urban air sample with that of a surrogate laboratory smog mixture containing pure hydrocarbons, and found the reactivity for the urban air sample to be about 40 percent greater than that of the surrogate. Those authors suggested that various aldehyde species were contributing to the reactivity of the urban sample. Killus and Whitten (1982) calculated that a carbonyl fraction of 0.09 was necessary to explain the additional reactivity. However, the emissions fraction of carbonyl groups might be less than this, since some of the excess reactivity would be due to carbonyls produced by previous photochemical reaction.

Dimitriades and Wesson (1972) reviewed available information concerning the relative levels of aldehydes and hydrocarbons found in automobile exhaust. In tests performed by the U.S. Bureau of Mines (Sawicki, Stanley, and Elbert, 1961; Dimitriades and Wesson, 1972), a mole fraction of total aldehyde per mole of hydrocarbon was calculated to range from 0.06 to 0.09. Other studies indicated greater variation, with mole fractions of aldehyde ranging from 0.07 to 0.35 (Oberdorfer, 1967) and

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* The term "reactivity" has acquired a variety of meanings in smog chemistry. In this context we define it as the oxidative production of peroxyl radicals, a process which then effects a conversion of NO to NO_2.

from 0.12 to 0.20 (Wadowski and Weaver, 1970). Dimitriades and Wesson (1972) concluded that total aldehyde levels in pre-1970 auto exhaust represented about 10 percent of total hydrocarbon on a molar basis and 5 percent on a carbon basis (the aldehydes being about 60 percent formaldehyde on a molar basis).

Altshuller and McPherson (1963) measured ambient concentrations of formaldehyde and acrolein. Acrolein was found to make up 10 percent to 15 percent of the concentration of formaldehyde, thus indicating the probable importance of carbonyl species other than simple aldehydes. Seizinger and Dimitriades (1972) identified numerous carbonyl compounds in automobile exhaust--notably acrolein, acetone, and the aromatic aldehydes. Although Altshuller and McPherson (1963) did not report aldehydes as a fraction of reactive hydrocarbon, the formaldehyde concentrations observed (0.01 to 0.115 ppm) were consistent with the 5 percent carbon fraction suggested by Dimitriades and Wesson (1972).

In an analysis of monitoring data for the Los Angeles area (Scott Research Laboratories, 1970), Killus et al. (1980) concluded that aldehyde emissions were similar to olefin emissions when calculated on a molar basis. If this assumption is made, the data given in this section indicate aldehyde emissions that range from 0.021 to 0.031 as a fraction of emitted reactive carbon.

Data are very sparse for emissions from vehicles having pollution-control devices. However, in a review of recent data, Bulon, Malko, and Taback (1978) found no major differences in the relative formaldehyde emissions from controlled and uncontrolled vehicles. Reported emission levels were fairly low in these studies: approximately 2 to 3 percent of total RHC. Note that total aldehyde emissions would be expected to be higher and total carbonyls higher still.

Hanst, Wong, and Bragin (1982) conducted a long-path infrared measurement study of Los Angeles smog. The study is noteworthy in several respects. One of the infrared absorbtion spectra used in the study was the so-called C-H band, which is a good measure of alkyl carbon, i.e., the measurement corresponds almost precisely to PAR in the Carbon-Bond Mechanism. Total NMHC can be estimated from PAR (assuming an additional proportion of olefinic and aromatic bonds) and other measured compounds can be expressed as a fraction of total NMHC. This is done in Table 5 for formaldehyde and ethene (C_2H_4).

The relative fraction of formaldehyde to NMHC would be expected to increase during the daylight hours as photochemistry produces formaldehyde from other compounds. As can be seen in Table 5, this is what is observed. Similarly, ethene is destroyed by photochemical reaction and its relative fraction decreased during the day.

TABLE 5. POLLUTANT CONCENTRATIONS MEASURED BY A LONG-PATH INFRARED STUDY OF LOS ANGELES SMOG

Time	NMPC* (ppbC)	H_2CO (ppb)	H_2CO/NMHC**	C_2H_4 (ppb)	C_2H_4/NMHC**
0635	870	29	0.024	31	
0710				31	0.043
0720	1090	33	0.022		
0810	780	33	0.030		
0840				17	0.032
0900				20	0.04
0930	720	40	0.040		
1010				20	0.04
1030	720	37	0.037		
1100					
1155				19	0.038
1220	720	42	0.042		
1315	700	42	0.043		
1345				24	0.043
1420	900	56	0.044		
1445				15	0.041
1510	740	42	0.040		
1535				12	0.023
1620				10	0.019
1645	750	37	0.035		
1705				9	0.019
1735	620	32	0.037	7	0.016
1840	500	34	0.049		
1905				13	0.036
1945	530	25	0.034		
2010				16	0.036
2045	760	26	0.024		
2115				23	0.040
2145	980	24	0.018		
2300				25	0.036
0045				21	0.031
0110	980	26	0.019		
0245	1210	33	0.020		
0305				23	0.034
0445					
0505	720	34	0.034		
0605	660	36	0.039		

Continued

TABLE 5. Concluded.

Time	NMPC* (ppbC)	H_2CO (ppb)	H_2CO/NMHC**	C_2H_4 (ppb)	C_2H_4/NMHC**
0630				26	0.032
0710	1640	47	0.02	63	0.055
0815	1610	49	0.022		
0840				38	0.036
0903	1440	59	0.029		
0930				33	0.034
0950	1320	58	0.031		
1020				27	0.030
1045	1210	48	0.028		
1215 p.m.				20	0.027
1240	1020	48	0.034		

* Nonmethane paraffinic carbon. The CPIR system used by Hanst, Wong, and Bragin measures $-CH_2^-$ and $-CH_3$ groups which correspond almost exactly to PAR in the Carbon-Bond Mechanism (some unreactive hydrocarbons such as ethane and propane would be included in NMPC).

** Nonmethane hydrocarbon is estimated as NMPC x 1.4, assuming an additional loading of aromatic and olefinic carbon. Ratios are expressed as relative carbon fraction.

The relative fraction of emissions for HCHO and ethene, may best be estimated from the nighttime values. Thus, formaldehyde seems to be about 2 percent of emissions (as carbon) and ethene is 3 to 4 percent of NMHC (as carbon). The ethene fraction is completely consistent with the three examples noted in this chapter; the formaldehyde fraction corroborates the measurements of Grosjean et al. (Example 3)

Given the information presented in this chapter we may prepare an outline of plausible carbonyl emissions in an urban emissions inventory. Formaldehyde emissions alone account for perhaps 2 to 6 percent of the carbon emitted in automobile exhaust; however, formaldehyde would account for only 1 to 4 percent of total emitted reactive carbon, since other emission processes (e.g., evaporation) seldom emit aldehyde per se.

Adding other aldehydes to formaldehyde increases our estimate of carbonyl emissions by approximately 50 percent (since formaldehyde represents 60 percent of aldehyde emissions on a molar basis). The addition of other carbonyl compounds (e.g., acetone, acrolein, and benzaldehyde) increases the carbonyl emissions rate still further, to perhaps twice that of emitted formaldehyde. Finally, surrogate carbonyl in the CBM accounts for 1 to 2 percent of emitted carbon.

In the CBM, carbonyl emissions as a fraction of total reactive carbon emissions would be approximately 5 percent, which is in agreement with the assumptions used in previous EKMA studies. With the onset of photochemical smog formation, the carbonyl fraction increases because of oxidation of reactive hydrocarbons to aldehydes, ketones, glyoxals, and so forth. This process eventually reaches a photochemical equilibrium in which carbonyl carbon can represent as much as 15-25 percent of reactive carbon.

Representativeness of the Los Angeles Area

Because the three examples given in this section are all taken from Los Angeles, the question arises as to whether the hydrocarbon speciation found in Los Angeles is representative of urban hydrocarbons in general. The available evidence suggests that urban hydrocarbons do not vary widely in reactivity or composition. In a survey of hydrocarbon compositions measured in different urban areas, the range of hydrocarbons was found to be fairly small (see Table 6).* Since the observed variations in composition also reflect measurement variance, the actual city-to-city variability is likely to be even less than that reflected in Table 6.

When compared to the hydrocarbon composition found in other urban areas, the Los Angeles 1981 speciation does appear to be somewhat depleted

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* Killus and Whitten, 1982.

TABLE 6. RANGES OF URBAN HYDROCARBON COMPOSITIONS (Source: Killus and Whitten, 1982).

Bond Type	Range	Recommended Value
ETH	0.02 - 0.11	0.04
OLE	0.02 - 0.07	0.03
ARO	0.10 - 0.4	0.19
PAR	0.5 - 0.70	0.58
CARB	0.03 - 0.10	0.05
Unreactive* Nonmethane Hydrocarbons	0.05 - 0.22	0.15

* Killus and Whitten (1982) reported the speciation as normalized to reactive hydrocarbons (RHC). The data in this table have been modified to reflect the inclusion of the unreactive hydrocarbon components.

in olefins and somewhat enriched in aromatics. This feature may be traced to the effects of rules instigated to regulate the reactivity and composition of gasoline in southern California. For example, the bromine number of gasoline sold in the South Coast Air Basin may not exceed 30.* The result of this and other measures to reduce the olefin content of emitted hydrocarbons in Los Angeles has been to increase the aromatic fraction as well. Apart from this difference, it is probable that, nationwide, the composition of urban hydrocarbons is similar to compositions for Los Angeles noted in this chapter. In any case, in the absence of an extensive study to determine the composition of hydrocarbons in a particular area, the default values noted in Table 5 should be used. The default composition is suggested as a good first estimate for any U.S. city. Killus and Whitten (1982) show how hydrocarbon splits from several cities fall within the range recommended in Table 5.

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* The bromine number corresponds to the number of grams of bromine (Br_2) that will react with 100 grams of gasoline. The test is exactly specific to the proportion of olefinic bonds in the gasoline (although it cannot distinguish between internal and terminal olefins). A bromine number of 30 corresponds to an olefin bond fraction of 0.054. In practice, the bromine number of gasoline in Los Angeles has been reduced to 6-14, corresponding to an olefin fraction of 0.01 to 0.025. Note that ethene is not a constituent of gasoline, but is instead a combustion product and is emitted from certain industrial processes. Ethene is also a plant hormone, i.e., it is emitted biogenically.

SECTION 3

PARAMETERS AND LUMPED RATE CONSTANTS IN THE CBM-III/EKMA

As noted previously, any generalized mechanism compact enough to be used in atmospheric simulation models will require some averaging of reaction rate constants and will probably include some parametric assumptions. The CBM-III/EKMA contains the following reactions that depend on hydrocarbon composition and assumptions about the physical state (e.g., surface to volume ratio and surface type, spectrum of incident light) of the smog system:

- Rate constant for the heterogeneous reaction of N_2O_5 with water (parameterized in Reaction 12)
- Lumped rate constants for radical-hydrocarbon reactions (Reactions 16-25, 34-36, 56, 57, 66, 70)
- Nitrate formation rate for alkylperoxy radical with NO (Reaction 31)
- Alkoxy decomposition parameter (A-factor, Reactions 29, 30)
- Rates of formation of phenolic compounds relative to ring opening (Reactions 56, 57)
- Yield of alkylated α-dicarbonyls from aromatics (Reactions 60-61)
- Photolysis rates, especially for carbonyls (Reactions 36, 37)

In this section, we describe how these rate constants and parameters can be estimated and recommend values on the basis of hydrocarbon composition data given in the previous section.

Decay of NO_2 and Ozone

Reaction 12 in the CBM-III/EKMA is a parameterization of the more complicated reaction scheme:

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad (3\text{-}1)$$

$$N_2O_5 \rightarrow NO_3 + NO_2 \qquad (3\text{-}2)$$

$$N_2O_5 + H_2O \xrightarrow{\text{surface}} 2\ HNO_3 \qquad (3\text{-}3)$$

The species N_2O_5 is assumed to be in steady state and the rate constant for Reaction 12 is computed on that basis. The daytime dynamics of N_2O_5 formation and destruction depart from the steady-state approximation at high concentrations of NO_2 and O_3 (NO_2 and O_3 > 0.3 ppm). However, this circumstance is rare. Also, N_2O_5 may not be correctly treated in steady state at night because its steady-state concentration might exceed the NO_x concentration.

Because Reaction 3-3 is surface-dependent, its estimation for atmospheric circumstances is difficult. Ideally, the destruction of N_2O_5 in this manner should be treated as a surface deposition. This is beyond the current capability of OZIPM/EKMA. However, a simple first-order loss, parameterized in Reaction 12, is acceptable because its effects on daytime simulation results is fairly minor in the atmosphere.

Platt et al. (1980) measured the lifetime of the NO_3 radical in the Los Angeles atmosphere at night. From these measurements, it is possible to place upper limit values on Reaction 3-3 and Reaction 12 in the CBM-III/EKMA. The daytime value for Reaction 3-3 is likely to be less than the value at night due to a reduction in the surface-to-volume ratio with the daytime increase in mixing depth. The maximum lifetime of the NO_3 radical reported by Platt et al. was approximately one minute, from which a value of 2.25×10^{-6} ppm^{-2} min^{-1} was derived for Reaction 3-3, or a value of 1.3×10^{-3} ppm^{-2} min^{-1} for the pseudo-third-order Reaction 12.

The water can also be incorporated into the reaction and rate constant, making a pseudo-second-order reaction of NO_3 with NO_2. To do this, we recommend a water level of 20,000 ppm, which corresponds to a dew point of about 65 F, or 50 percent relative humidity, at 85 F. The pseudo-second-order rate constant for Reaction 12 would then be 26.0 ppm^{-1} min^{-1}.

Paraffins--OH Rate Constant

In a typical urban mix of hydrocarbons, approximately 80 percent of the total alkyl groups are contained in alkane (paraffin) molecules (see Section 2). The work of Greiner (1970) suggests that the reactivity of most alkanes (C > 3 apart from cyclopropane, cyclobutane, and molecules containing a

tertiary-butyl group) can be described in terms of the number of primary, secondary, and tertiary C-H bonds. Darnall et al. (1978) and Atkinson et al. (1979) suggest a modification of Greiner's formula:

$$K_{OH} = 1.01 \times 10^{-12} N_1 e^{823/T} + 2.41 \times 10^{-12} N_2 e^{-428/T}$$

$$+ 2.1 \times 10^{-12} N_3 \text{ cm}^3 \text{ molecule}^{-1} \text{sec}^{-1}$$

where N_1, N_2, and N_3 are the number of primary, secondary, and tertiary C-H bonds. At 298 K, this equation becomes

$$283\ C_p + 1696\ C_s + 3110\ C_t \text{ ppm}^{-1} \text{min}^{-1},$$

where C_p, C_s, and C_t are the number of primary, secondary, and tertiary carbons.

Because the creation of a tertiary carbon involves a branching that must generally terminate in a primary carbon group, the effect of branching on hydroxyl reactivity is negligible in the modified Greiner formulation:

$$2C_s \cong C_p + C_t \quad .$$

Thus, the overall OH-reactivity per carbon atom is similar for most alkanes, increasing only gradually with increasing carbon number.

The average carbon number for paraffins in the three example mixes given in Section 2 may be calculated as 5.3, 5.1, and 5.5, for examples 1, 2, and 3, respectively. From the modified Greiner formula, we may calculate reaction rate constants with hydroxyl to be 1162 ppm^{-1} min^{-1}, 1142 ppm^{-1} min^{-1}, and 1182 ppm^{-1} min^{-1} per carbon atom for the paraffin molecules in these three mixes.

Roughly 20 percent of the alkyl carbon in the three example mixes is to be found in nonparaffin molecules, primarily aromatics. The shorter alkyl carbon number in these molecules reduces the average alkyl carbon number for the three mixes to 4.4, 4.0, and 4.8, respectively. If aromatic alkyl carbon followed the modified Greiner formula, this would reduce the average OH-PAR rate constant. However, the aromatic ring appears to activate the alkyl group to H atom abstraction (see Table 7). Overall, the aromatic linked alkyl carbon seems to be slightly more reactive than the average paraffin molecule. The calculated average OH-PAR rate constant for all three mixes is very close to 1200 ppm^{-1} min^{-1} and we recommend that value.

TABLE 7. OH ABSTRACTION PER ALKYL CARBON FOR SEVERAL AROMATIC MOLECULES. (Calculated from data contained in Atkinson et al., 1979).

Compound	OH Abstraction Rate per Alkyl Carbon Atom (ppm^{-1} min^{-1})
Toluene	1536
Ethylbenzene	1593
o-xylene	2145
m-xylene	720
p-xylene	803
1,2,3-trimethylbenzene	583
1,2,4-trimethylbenzene	600
1,3,5-trimethylbenzene	624

Paraffins--Nitrate Formation

Long-chain paraffin molecules undergo a nitrate formation reaction (Reaction 31) that depends on the length of the alkyl chain (see Table 8, Figure 1). The distinction must be made here between alkyl chain length and carbon number. A branched hydrocarbon such as 2,3-dimethyl butane seems to have a nitrate formation yield more similar to n-butane than to n-hexane (private communication, Carter, 1983).

For this reason we base our estimate of the relevant rate constant on the alkyl chain length of our typical urban mixes. For our examples the calculated alkyl chain is between 4.0 and 4.4. The ratio of Reaction 31 to the sum of Reactions 29 to 31 would, according to Atkinson et al. (1982), be 0.077 to 0.1, for $RO_2\cdot$ radicals (modeled as MeO_2 in the CBM-III/EKMA) derived from paraffins. Since some MeO_2 radicals are derived from aldehyde oxidation, which results in short alkyl chains, we recommend the lower value of 900 ppm^{-1} min^{-1} for the rate constant of Reaction 31. This number also provides simulated nitrate levels close to measured values in smog chamber experiments using urban mixes.

Alkoxy Radical Decomposition and Isomerization (A-factor)

When an alkylperoxy radical ($RO_2\cdot$) reacts with NO it generally forms NO_2 plus an alkoxy radical (RO·):

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot$$

The alkoxy radical may then react in a number of ways, either with oxygen to form aldehydes or ketones (CARB) only, or to reform an $RO_2\cdot$ radical by a number of pathways. For a discussion of alkoxyl chemistry, the reader is referred to Whitten, Killus, and Hogo (1980). In the CBM-III/EKMA, the RO· radical is treated implicitly. Alkoxy radical reaction with oxygen is treated in Reaction 29. Alkylperoxy reformation (through decomposition or isomerization), is treated in Reaction 30.

The total number of alkylperoxy radicals formed per reaction with OH is termed parameter or factor "A" in the CBM-III/EKMA:

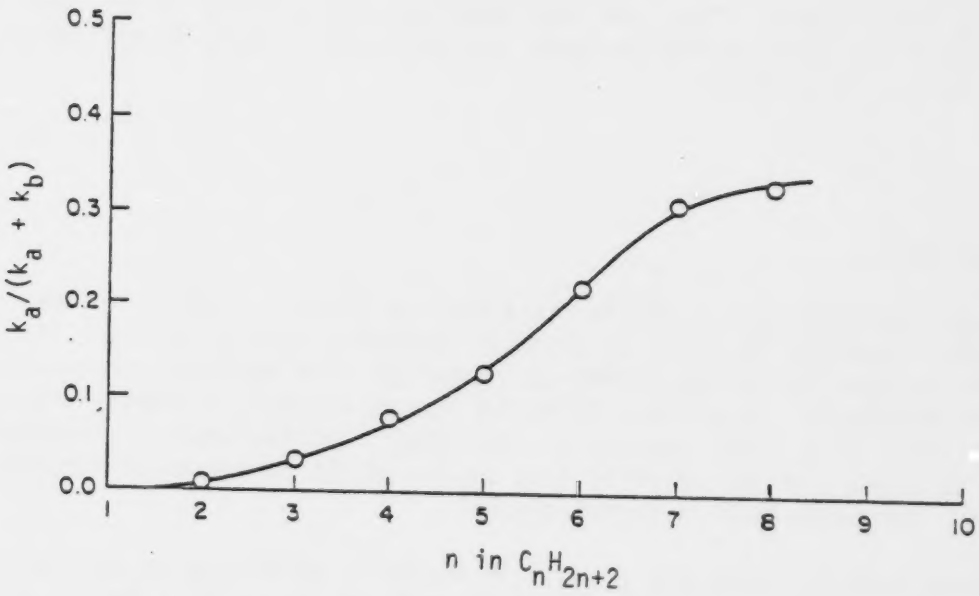
$$K_{(29)} = [12000 - K_{(31)}] \frac{A - 1}{A} \text{ ppm}^{-1} \text{ min}^{-1} \quad ,$$

TABLE 8. Fractional yields of alkyl nitrates in the NO_x-air photooxidation of C_2 through C_8 n-alkanes.

n-Alkane	Δ[alkyl nitrate]/-Δ[n-alkane][a)]
Ethane	0.010
Propane	0.036
n-Butane	0.077
n-Pentane	0.128
n-Hexane	0.22
n-Heptane	0.31
n-Octane	0.33

a) Corrected for loss processes of alkyl nitrates due to reaction with OH radicals

Source: Atkinson et al. (1982)



Source: Atkinson et al. (1982)

FIGURE 1. Plot of the rate constant ratio $k_a/(k_a + k_b)$ against carbon number in the n-alkane series. (k_a is the rate constant for nitrate formation from RO_2 + NO reactions and k_b is the rate constant to alkoxy radicals and NO_2).

$$K_{(29)} + K_{(30)} + K_{(31)} = 12000 \text{ ppm}^{-1} \text{ min}^{-1} \quad .$$

For a typical mix of hydrocarbons, A was determined to be 1.5, based on experimental evidence and known detailed chemistry (Killus and Whitten, 1980). Since a value of 900 is recommended for $K_{(31)}$, $K_{(29)}$ has a recommended value of 3700 ppm^{-1} min^{-1} and K_{30} = 7400 ppm^{-1} min^{-1}.

Olefins

The radical reaction rate constants for monoalkylated (terminal) olefin bonds are nearly invariant for most of the compounds in which they occur (see, for example, Ohta, 1983). Thus, the rate constants for olefins in the CBM-III/EKMA, which are derived from propene, are expected to apply to all monoalkylated olefins (1-olefins).

Aromatics

OH Reaction Rate--

Hydroxyl reaction with aromatic rings has two product channels in the CBM-III/EKMA. Reaction 60 leads to phenolic compounds such as cresols; it also mimics to some degree the formation of phenols from subsequent reactions of aromatic aldehydes. Otherwise, formation of the aromatic aldehydes are treated in alkyl group (PAR) chemistry. The other reaction channel (Reaction 61) leads to opening of the aromatic ring and to prompt formation of alkylated α-dicarbonyl compounds such as methyl glyoxal.

The rate constant averaging problem in aromatics chemistry is more severe than for olefins and alkyl groups. The rate constant varies by a factor of 10 between monoalkylated benzenes such as toluene and the most reactive trimethyl benzenes (e.g., the 1, 3, 5 isomer). Fortunately, most of the aromatics have OH rate constants that are within a factor of 2 of the average value.

As we note in Section 2, atmospheric measurements tend to neglect compounds that exist at low concentrations, but that can nevertheless constitute an appreciable fraction of total hydrocarbon reactivity. This is especially true for higher molecular weight compounds such as aromatics, particularly the di- and tri-alkylated compounds for which many isomers exist. Since these compounds are of greater than average reactivity, compound reactivity averages calculated from ambient data will tend to underpredict the true average reactivity.

This underprediction problem is especially evident in Example 2 (Section 2), which does not contain data for trimethylbenzenes or ethyltoluenes, compounds known to occur in urban emissions. Accordingly, we have used only Examples 1 and 3 to calculate average OH rate constants for aromatics. Using values derived from Atkinson et al. (1979), for the individual compounds, and subtracting the contribution of H atom abstraction from the alkyl substituents, we obtain values of 22,500 ppm^{-1} min^{-1} and 18,150 ppm^{-1} min^{-1} for Examples 1 and 3, respectively. These numbers correspond to the sum of Reactions 56 and 57 in the CBM-III/EKMA.

The formation pathway ratios of phenolics to ring opening in Killus and Whitten (1982) are based on toluene and m-xylene. The formation of phenolics from toluene is much greater than for the xylenes (possibly excepting o-xylene) and is probably greater than for most other aromatics. Thus, we reduce the phenolic pathway fraction somewhat for the aromatic mixture. The recommended value for Reaction 56 is 6,000 ppm^{-1} min^{-1}, and for Reaction 57 is 14,500 ppm^{-1} min^{-1}, which sum to the approximate average aromatic reactivity for Examples 1 and 2.

Yield of Alkyl-Substituted α-dicarbonyls--

Ring opening in alkyl benzene photooxidation systems generally leads to at least one alkyl-substituted α-dicarbonyl (e.g., methyl glyoxal). For monoalkylated benzenes such as toluene, only a single alkyl dicarbonyl may result. For di- and trialkylated aromatics a greater yield is possible.

There is currently some question as to whether the formation of these additional α-dicarbonyl products is prompt or is delayed by the formation of an intermediate unsaturated product, e.g., an olefinic dialdehyde (see Atkinson et al., 1980; Killus and Whitten, 1982). Recent smog chamber studies (Bessemer 1982; C. Spicer, private communication) indicate that the yield of the dial products is low. Whitten, Killus, and Johnson (1983) suggest that the formation of the additional alkyl α-dicarbonyl products is prompt--consistent with the observations of a low dial yield.

Additional products from aromatic oxidation in the CBM-III/EKMA are represented by the species APRC (Aromatic Product Carbon). For monoalkylated benzenes, the product of APRC is two glyoxal molecules, which are represented in the CBM-III/EKMA as CARB + CO. Dialkylated benzenes yield glyoxal plus an alkyl α-dicarbonyl (DCRB), while trialkylated benzenes give two alkyl dicarbonyls or one glyoxal plus a dialkyl dicarbonyl (e.g., biacetyl). The formation of dialkyl dicarbonyls is a relatively minor pathway, however.

The ratio of APRC products (Reactions 60 and 61) is determined from the average number of alkylation sites in the aromatic mix. In our three

examples, the average alkylations are 1.69, 1.4, and 1.5, respectively. For an average number of alkylations equal to 1.5, Reaction 60 equals Reaction 61. We recommend 10^4 min^{-1} for both reactions. If the secondary formation of alkyl dicarbonyls is delayed by the existence of an intermediary dial, Reactions 60 and 61 would be slower and would depend on OH concentration. For a typical level of OH, a pseudo-first-order rate appropriate to simulate slow APRC decay would be 0.004 min^{-1} for the sum of Reactions 60 and 61. The faster reactions just noted are more likely, however, given our current knowledge of the ring opening process.

Carbonyls

Oxygenated compounds containing a carbonyl group (aldehydes and ketones) are important intermediate species in smog chemistry. In the CBM-III/EKMA, most of these compounds are lumped into a single species--CARB. The relative amounts of the carbonyl compounds that make up the CARB group determine the specific reaction rate constants for Reactions 34-38 in the CBM-III/EKMA. Reactions 37 and 38 are photolysis reactions and are discussed in Section 4. We now discuss the appropriate composition of CARB and the determination of Reactions 34-36.

Mix of Carbonyls--

The initial (morning) composition of the carbonyl category in the CBM-III/EKMA is strongly influenced by two factors--fresh emissions and the composition of the most reactive hydrocarbons, which we have taken as surrogate carbonyls in the CBM-III/EKMA.

The data of Grosjean et al. (1981), (Example 3, Section 2) for carbonyls, indicates an initial ratio of formaldehyde to total aldehydes of about 0.6. On the other hand, surrogate carbonyls are primarily internal olefins, which produce higher aldehydes rather than formaldehyde. Taking immediate production of higher aldehydes from reactive olefins into account, the initial formaldehyde fraction would be very close to 0.5. This is supported by a more extensive data set (Grosjean, 1982), which also indicates a morning formaldehyde fraction of 0.5 or less. The data of Grosjean (1982) also contains information on ketone concentrations, indicating them to be of negligible (< 5 percent) importance in the morning hours.

Subsequent photochemical reaction tends to raise the amount of formaldehyde relative to other aldehydes. This is because the higher aldehydes react more rapidly with OH than does formaldehyde, and when reaction occurs, formaldehyde is formed as the end product. This phenomenon is also apparent

in ambient data for aldehydes. The overall average formaldehyde fraction of total aldehydes in the data of Grosjean (1982) is about 0.6.

Photochemical reaction also produces glyoxal, primarily from aromatic oxidation. Glyoxal is similar to formaldehyde in its reactivity to OH (Plum et al., 1983) and in its products. (It photolyzes primarily to stable products, however.)

The average ratios of formaldehyde, higher aldehydes, and glyoxal over the entire lifetime of a hydrocarbon can be estimated. The estimation procedure is too lengthy to describe in detail, but it involves an analysis of the structure of the hydrocarbon and determination of which structures in the hydrocarbon may yield which products. For example, formaldehyde is primarily produced by $-CH_3$ groups in most molecules, while glyoxal results from non-alkylated carbon-carbon pairs in aromatic molecules.

When the carbonyl estimation procedure is applied to the hydrocarbon mxitures in Section 2, we obtain the following fractions:

Formaldehyde	0.6
Higher Aldehydes	0.25
Glyoxal	0.1
Ketones*	0.05

The effects of the changing mix of carbonyls is seen primarily in the reactions of CARB with OH (Reactions 34-36). The ketone fraction appears to remain quite low; the rate constant for Reaction 34 remains around 100 $ppm^{-1}min^{-1}$. Reactions 35 and 36 change substantially with photochemical reaction. With the 50/50 mixture of formaldehyde and higher aldehydes that is seen in the early morning, reaction 35 would have a value of 7000 $ppm^{-1}min^{-1}$ and Reaction 36 would be 12,000 $ppm^{-1}min^{-1}$. As chemical reaction proceded toward the average composition, these reaction values would become 10,500 $ppm^{-1}min^{-1}$ and 6000 ppm^{-1} min, respectively.

While the overall rate of reaction does not change significantly as reaction proceeds, the relative production of peroxyacyl and hydroperoxyl radicals changes substantially. The effect of this change is seen primarily in the production of PAN; ozone formation is little affected. Empirically, PAN formation is best simulated by a ratio of Reactions 35 and 36 that is midway between the initial and full oxidation average values: 9000 $ppm^{-1}min^{1}$ for Reaction 35 and 8200 $ppm^{-1}min^{-1}$ for Reaction 36. This corresponds to the following mix of carbonyls:

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* The 0.05 fraction is based upon the measurements of Grosjean, 1982.

Formaldehyde	0.55
Higher Aldehydes	0.35
Glyoxal	0.05
Ketones	0.05

The effects of the carbonyl mix on photolysis will be discussed in the next section.

SECTION 4

PHOTOLYSIS RATES

As the name implies, photochemical smog is activated by sunlight, specifically ultraviolet light. As may be seen in Figure 2, different chemical species are sensitive to different portions of the solar spectrum, making relative photolysis sensitive to factors that alter the solar spectrum, e.g., solar zenith angle. The CBM-III/EKMA considers the photolysis of five species: NO_2, carbonyls (CARB), α-dicarbonyls (DCRB), nitrous acid (HONO) and ozone O_3. Since the photolysis of NO_2, often referred to as k_1, is the most studied and best understood photolysis reaction, we discuss this reaction first.

PHOTOLYSIS OF NO_2 (k_1)

The computer program OZIPM with which EKMA/CBM-III calculations are performed, calculates the rate of NO_2 photolysis based on the algorithm of Schere and Demerjian (1977). The calculations of Schere and Demerjian, were based on actinic irradiance values calculated by Peterson (1975) using a radiative transfer model developed by Dave (1972). From these actinic fluxes, NO_2 photolysis rates were calculated from available absorbtion and quantum yield data.

The calculations of Schere and Demerjian were updated in 1980 (Demerjian et al., 1980) and rates were reported as a function of height (Table 9). Note that there is good agreement between the values calculated in OZIPM using the Schere and Demerjian algorithm, and the column averaged values for the first two levels (0 - 0.36 km) of the light scattering model (Demerjian et al., 1980).

In addition, Table 9 contains NO_2 photodissociation rates as calculated by Duewer et al., (1974), which are also based on radiative transfer model results, and Killus et al., (1977/1980), which were derived from measurements of volumetric UV flux and calibrated to direct measurements of NO_2 photolysis. Note that the discrepancy between these various methods for the

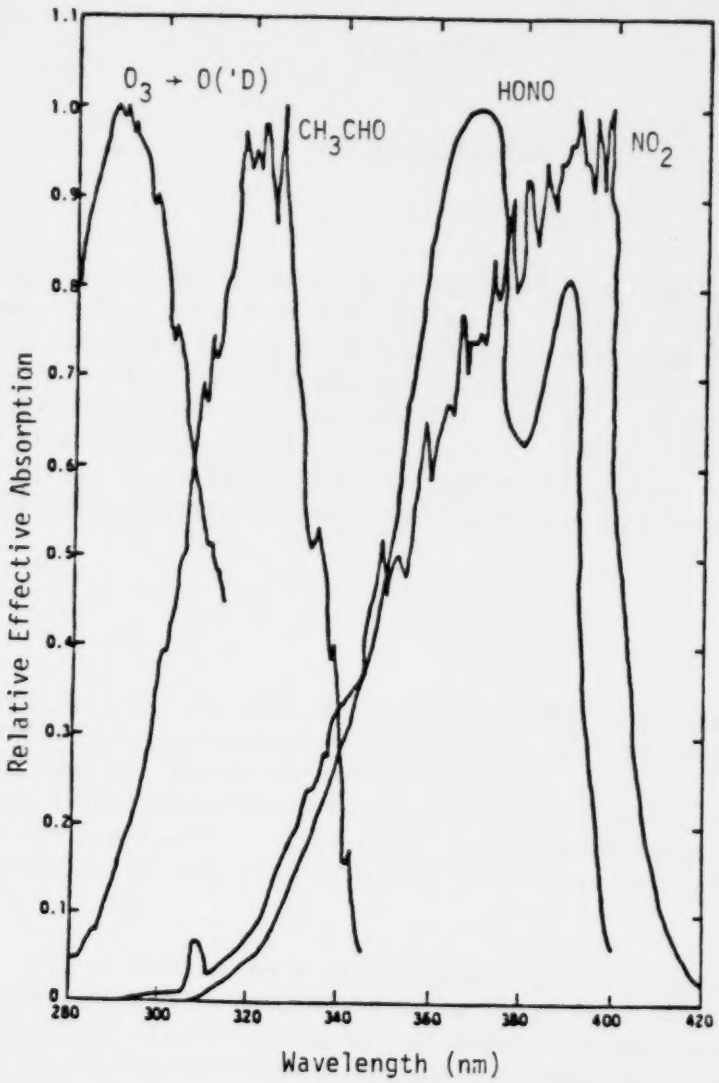

FIGURE 2. Product of flux and cross-section for photolysis of ozone, acetaldehyde, HONO, and NO_2. (Source: Whitten et al., 1979).

TABLE 9. NITROGEN DIOXIDE PHOTOLYSIS RATES (k_1) ($k_1 \times 10^3\ s^{-1}$) AS A FUNCTION OF SOLAR ZENITH ANGLE

Zenith Angle (degrees)	Leighton*	Demerjian 1977**	Demerjian et al., 1980				Killus et al. 1977/1980†	Duewer et al. 1974††
			Surface	Level 1 (0.15 km)	Level 2 (0.36 km)	Level 3 (0.64 km)		
0	10.0	9.64	8.88	9.42	9.9	10.36	9.38	12.0
10			8.81	9.35	9.83	10.3		
20	9.67	9.33	8.59	9.13	9.64	10.12	9.33	11.5
30			8.21	8.78	9.29	9.78		
40	8.46	8.25	7.61	8.2	8.73	9.23	7.3	10.0
50			6.72	7.33	7.87	8.38		
60	5.93	5.94	5.48	6.01	6.55	7.06	4.2	6.7
70			3.56	4.06	4.54	5.0		
78			1.75	2.04	2.35	2.67		
86			0.38	0.42	0.47	0.52	0.47	

* Calculated by Demerjian and Schere (1975) using Leighton's (1961) actinic fluxes.

** Used in OZIPM.

† Used in Urban Airshed modeling studies.

†† Used in LIRAQ grid model.

determination of k_1 is small, generally less than 20 percent. This is also demonstrated in Figure 3 where the surface value of NO_2 photolysis calculated from Demerjian et al. (1980) is compared to the empirically calibrated methods involving UV and TSR data (Whitten, Killus, and Johnson, 1983).

Natural factors may cause some expected deviation from the calculated solar function. Cloud cover obviously has some effect (evident in Figure 3) but correcting for clouds is a difficult and cumbersome procedure. Since overcast days do not usually coincide with smog episodes, we do not recommend any attempt at treating cloud effects.

Atmospheric turbidity (including the effects of smog itself) has been shown to cause as much as a 30 percent decrease in surface irradiance (Peterson et al., 1980). However, Killus et al. (1980) note that turbidity redistributes light in the mixed (polluted) layer, and that the effect on collumn-averaged irradiance is less than 10 percent.

Finally, irradiance increases with elevation. Anderson et al. (1977) noted a +15 percent correction for NO_2 photolysis in photochemical calculations for Denver, Colorado. However, unless the elevation of the urban area is extreme, the correction becomes negligible.

CARBONYL PHOTOLYSIS

Photolysis of carbonyl compounds (CARB) in the CBM-III/EKMA is a major source of free radicals that drive the hydrocarbon oxidation process. Photolysis of CARB can be treated in two ways: either as a ratio to NO_2 photolysis, or as a ratio to some species whose photolysis is treated explicitly in OZIPM, e.g., HCHO. If this latter technique is used, the species name "CARB" must be replaced with the photolytic species identified in OZIPM.

Because the ratio of carbonyl photolysis to NO_2 photolysis depends fairly strongly on solar zenith angle, the daily average ratio depends on latitude and time of year. In order that OZIPM may make these corrections automatically, we recommend the second method for treating the photolysis of CARB, which involves replacing the species name with "HCHO." The ratio used for "HCHO" (nee CARB) photolysis in OZIPM, will depend on the species mix of carbonyls (discussed in Section 3) and the photolysis of the various carbonyl species produced (formaldehyde, higher aldehydes, glyoxal, and ketones). We discuss the photolysis of these compounds next.

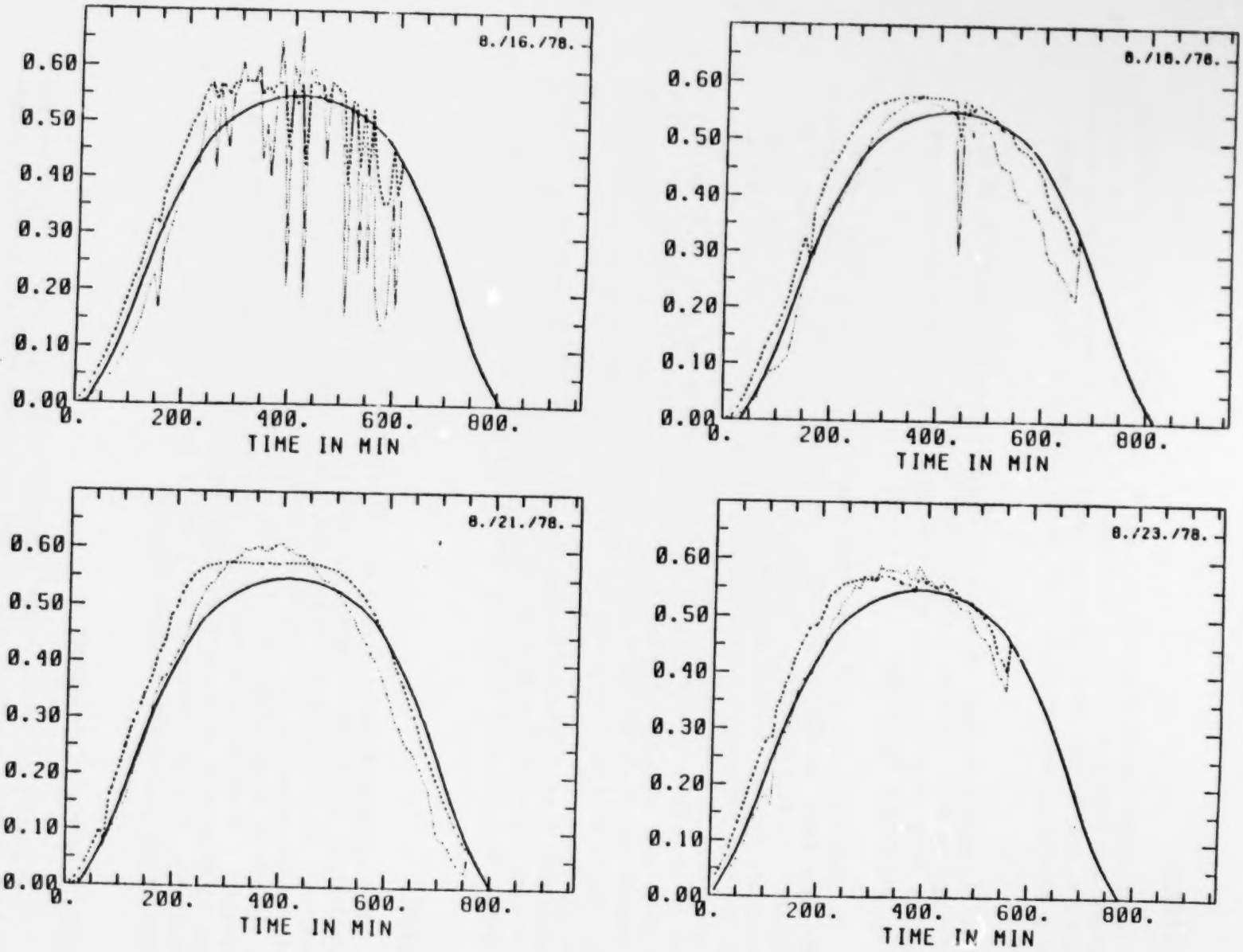

FIGURE 3. NO_2 photolysis (K_1) calculated from the algorithm of Demerjian et al., 1980 (solid lines) compared to photolysis derived from UV data (dashed lines) and TSR data (dotted lines).

Formaldehyde

Formaldehyde (HCHO) photolysis in OZIPM is based on the rates determined by Schere and Demerjian (1977). Photolysis of HCHO to both stable and radical products is considered; photolysis to stable products has a negligible effect on smog chemistry, whereas photolysis to radicals is of overwhelming importance.

In the update to their recommended photolysis rates, Demerjian et al. (1980) applied newer quantum yield information that substantially reduced the suggested photolysis of HCHO to stable products and somewhat increased the radical yield (see Table 10).

The photolysis rates of Schere and Demerjian (1977) and Demerjian et al. (1980) were based on HCHO absorbtion cross sections taken at elevated temperatures (Calvert et al., 1972). Recently, Bass et al., (1980) reported room temperature absorbtion cross sections for HCHO that were considerably lower than the high temperature data. Applying these new cross sections to the spectral data of Demerjian et al. (1980), we calculated a decrease in the rates of photolysis to radicals of 32 percent, and a decrease of 35 percent in the photolysis of stable products. This lower photolysis rate has been tested in simulations of formaldehyde under atmospheric conditions (including natural sunlight) by Whitten (1983), and was found to best reproduce the experimental $HCHO/NO_x$ data. The radical photolysis rate of pure formaldehyde in the OZIPM program should be multiplied by 0.81 to account for recent quantum yield and absorbtion cross-section data and for the increase in photolysis with height. The correction factor for photolysis to stable products is 0.37.

Glyoxal

Glyoxal photolyzes at a rate that is similar to the overall rate of formaldehyde photolysis (Plum et al., 1983), but the products of glyoxal photolysis seem to be mainly stable compounds. Carbon monoxide (CO) and H_2 are the main products, but some formaldehyde is also formed. The conversion of glyoxal to formaldehyde and its subsequent photolysis to radicals does represent a minor source of radicals. We estimate this source to be equivalent to 10 percent of the rate of formaldehyde photolysis to radicals. Conversely, glyoxal photolysis to H_2 and CO occurs at nearly twice the rate of formaldehyde photolysis to these compounds.

Higher Aldehydes/Acetaldehyde

The photolysis of the higher aldehydes under atmospheric conditions has not been studied as extensively as that of formaldehyde and is highly uncertain. Typically, acetaldehyde is taken to be representative of the higher aldehydes; estimates of the photolysis rate of acetaldehyde vary by more than a factor of 10 (see Table 11).

TABLE 10. FORMALDEHYDE PHOTOLYSIS RATIONS TO NO_2 ($\times 10^3$) AS A FUNCTION OF SOLAR ZENITH ANGLE

Solar Zenith Angle (degree)	Schere and Demerjian (1977)	Surface	Level 1 (0.16 km)	Level 2 (0.36 km)	Whitten 1983
(A) HCHO + hν→ H_2 + CO Ratio to NO_2 + hν					
0	9.68	5.55	5.70		3.76
10		5.53	5.68		3.75
20	9.52	5.45	5.60		3.70
30		5.31	5.46		3.60
40	9.01	5.09	5.23		3.46
50		4.78	4.90		3.26
60	7.98	4.29	4.44		2.99
70		3.74	3.79		2.59
78		3.28	2.85		2.29
86		2.96	2.34		2.18
(B) HCHO + hν→ H• + HCO• Ratio to NO_2 + hν					
0	3.7	4.20	4.39	4.49	2.71
10		4.17	4.36	4.45	2.70
20	3.59	4.05	4.24	4.34	2.61
30		3.85	4.03	4.13	2.48
40	3.25	3.56	3.73	3.81	2.28
50		3.15	3.30	3.38	2.01
60	2.58	2.61	2.76	2.81	1.64
70		2.03	2.12	2.10	1.25
78		1.53	1.62	1.57	0.91
86		1.16	1.19	1.28	0.52

TABLE 11. ACETALDEHYDE PHOTOLYSIS RATIOS TO NO_2 (X 10^3) AS A FUNCTION OF SOLAR ZENITH ANGLE

Solar Zenith Angle (degree)	Schere and Demerjian, 1977	Calvert and Horowitz, 1982*	Demerjian et al., 1980 (surface)†	Whitten, Killus, and Hogo, 1980**
0	0.734	0.358	4.22	0.916
10		~0.347	4.18	0.908
20	0.702	0.336	4.09	0.974
30		~0.300	3.89	0.816
40	0.594	0.263	3.61	0.734
50		~0.208	3.23	0.626
60	0.402	0.152	2.70	0.488
70		~0.106	2.13	0.348
78		0.06	1.66	0.234
86		~0.03	1.32	0.163

* Approximate values interpolated or estimated.

** Calculated from lower limit quantuum yields of Demerjian et al., 1980.

† Using upper limit quantuum yields.

Using the lower limit quantum yields of Demerjian et al. (1980), Whitten, Killus, and Hogo (1980) calculated acetaldehyde photolysis rates that were then empirically tested against outdoor smog chamber experiments (Whitten, and Johnson, 1983). We recommend these estimates, which indicate acetaldehyde photolysis at about 35 percent of formaldehyde photolysis. This estimate can be applied to the higher aldehydes with the caveat that the uncertainties are quite large.

Ketones

There is even less information concerning ketone photolysis under atmospheric conditions than is available for the higher aldehydes. Carter et al. (1979) estimated MEK photolysis to be similar to formaldehyde, whereas Whitten, Killus, and Johnson (1983) estimated the photolysis of acetone and MEK to be 6 and 12 percent, respectively, of formaldehyde photolysis, based on simulations of outdoor smog chamber experiments. The value estimated for MEK photolysis, however, is probably low, because the reaction rate constant used for MEK plus OH was faster than that indicated by recent measurements.

Calculations for MEK photolysis based on the spectrum of Demerjian and Schere (1977) and absorbtion and quantum yield information of Calvert and Pitts (1966) give an estimate of roughly 50 percent of formaldehyde photolysis. Using 15 percent as a lower limit and 50 percent as an upper limit, we derive 30 percent as our "best guess" for the ratio of ketone to formaldehyde photolysis.

PHOTOLYSIS OF CARBONYL MIX

Based on the mix of carbonyls described in Section 3, we can now estimate the correction factor to be used in OZIPM for "HCHO," (to replace CARB). These calculations are shown in Table 12. Because the number of radical products for carbonyl photolysis exceeds the number of products in a reaction for OZIPM, we split the photolysis into four reactions:

$$HCHO \rightarrow QQ \qquad 0.564 \tag{4-1}$$

$$QQ \rightarrow HO_2 + HO_2 + CO \qquad 8867\ min^{-1} \tag{4-2}$$

$$QQ \rightarrow MeO_2 + MeO_2 + X + XCO \qquad 1133\ min^{-1} \tag{4-3}$$

$$XCO \rightarrow X + CO \text{ fast } (10^4\ min^{-1}) \tag{4-4}$$

The factor 0.564 in Reaction 4-1 is the correction factor for photolysis calculated in Table 12. The ratio of Reactions 4-2 and 4-3 are determined by the relative amounts of HO_2 and RO_2 formed in the photolysis of the different carbonyl species. The use of the fictitious intermediate species "XCO" and QQ is due to the four-product species limit in OZIPM.

PHOTOLYSIS OF HONO AND OZONE

Photolysis of HONO under atmospheric conditions is rapid, and since it occurs at spectral wavelengths similar to NO_2 photolysis, the ratio is nearly constant, (0.18). However, this is 3.1 times the rate calculated internally by OZIPM and this correction factor should be applied to the rate constant.

Ozone photolyzes by two pathways; both must be included in OZIPM:

$$O_3 + \text{uv light} \rightarrow O^1D \qquad (4\text{-}5)$$

$$O_3 + \text{light} \rightarrow O^3P \qquad (4\text{-}6)$$

Ozone photolysis to O^3P is part of a "do nothing" cycle:

$$O_3 \xrightarrow{+\ \text{light}} O^3P \qquad (4\text{-}7)$$

$$O^3P + O_2 + M \rightarrow M + O_3 \qquad (4\text{-}8)$$

Photolysis to O^1D can be important under some circumstances, notably those approaching clean air. There is a correction factor of 0.71 for updating OZIPM ozone photolysis (based on Schere and Demerjian, 1977) to be consistent with Demerjian et al. (1980). However, direct measurements of this photolytic rate (Bahe et al., 1979) indicate a further correction of 0.75 for a combined correction factor of 0.53.

PHOTOLYSIS OF DCRB

The photolytic rate for dicarbonyls (DCRB) in Killus and Whitten (1982) was set equal to $\sim 0.04 \times K_1$, based on the known rate of photolysis for biacetyl. Recently, Plum et al. (1983) measured the photolysis rate of methylglyoxal and found it to be one-half that of biacetyl. Since methylglyoxal is the largest component of DCRB, we recommend $0.02 \times K_1$ as the

TABLE 12. CALCULATIONS FOR RATIOS OF CARBONYL PHOTOLYSIS TO FORMALDEHYDE PHOTOLYSIS IN OZIPM.

Species	Fraction of Carbonyl Mix	Ratio to Formaldehyde Photolysis
	For Radical Products	
Formaldehyde	0.55 x 1.0	0.55
Higher aldehydes	0.35 x 0.35	0.1225
Glyoxal	0.05 x 0.1	0.005
Ketones	0.05 x 0.35	0.0175
	Weighted average	0.696
	Correction for quantuum yield and absorbtion spectrum updates	0.78
	CARB ("HCHO") photolysis to radicals	0.564
	For Stable Products	
Formaldehyde	0.55 x 1.0	0.55
Higher aldehydes	0.35 x ~ 0	-
Glyoxal	0.05 x 2.0	0.1
Ketones	0.05 x ~ 0	-
		0.65
	Correction for quantuum yield and absorbtion spectrum updates	0.37
		0.240

photolysis rate for dicarbonyls. Also, on the basis of empirical data for yields of PAN in methylglyoxal NO_x systems, we recommend a 100 percent yield of ACO_3 from DCRB photolysis:

$$DCRB \xrightarrow{+ \text{ light}} ACO_3 + HO_2 + CO \quad (0.02 \times K_1)$$

5 INITIAL CONDITIONS, EMISSIONS, AND NMHC/NO_x RATIOS

Oxidant precursors enter the OZIPM/EKMA model in three ways:

Initial conditions
Emission
Transported air (including entrainment from aloft)

Transport can also introduce ozone directly into the model. Ozone and precursor concentrations due to transport can be derived from anthropogenic emissions upwind, which may be reduced if controls are applied. Alternatively, some ozone and precursor concentrations are due to the natural background of those species (e.g., stratospheric intrusion for ozone, biogenic and geogenic emissions for hydrocarbons). The magnitude and sources of background ozone and precursors are important topics in themselves and their treatment is discussed in Section 6.

In the EKMA methodology, initial conditions and emissions of ozone precursors are assumed to be linearly related (i.e., a reduction in emissions of NMHC or NO_x is assumed to result in a proportional reduction in the initial condition for those species). Also, whereas the emission inputs are derived from emission inventory information, initial conditions are derived from ambient monitoring data, which is also used to obtain ratios of NMHC to NO_x for use in the EKMA-isopleth-derived control strategy calculations.

To obtain a valid simulation of atmospheric photochemical processes, the proper concentration of ozone precursors must be supplied to OZIPM/EKMA. Furthermore, the initial conditions must be quantitatively related to post 0800 emissions; otherwise, the emissions/concentration assumption breaks down. In this section we discuss these two important issues: the use of ambient data and the relationship between measured concentrations and input emissions.

CONCENTRATIONS OF NMHC

If detailed, gas chromatographic (GC) determinations of nonmethane organic (NMOC) concentrations are available, (e.g., the three cases given in Section 2), then that information should be used to specify initial NMOC

concentrations and NMHC/NO_x ratios. However, gas chromatographs currently require intensive technical expertise; GC measurements are not usually available on a routine basis. Note also that even full GC speciation measurements usually have some residual "unknown" compounds whose speciation and reactivity must be assumed.

In the absence of chromatographic hydrocarbon data, some other method of obtaining NMOC concentrations must be used. To this end, a number of "NMHC measurement" devices have been marketed. These devices provide only an indirect measurement of NMHC in that they provide separate measurements of total organic compounds (TOC) and of methane (CH_4). The difference between the TOC and CH_4 measurements is (defined as) the NMOC measurement. Most NMOC analyzers are designed to perform the subtraction automatically and provide a direct NMOC output.

The TOC and CH_4 measurements are made with a flame ionization detector (FID), but several methods for separating the CH_4 from the TOC are in general use. Chromatographic analyzers use adsorbent columns to separate the CH_4 from all other organic compounds. These analyzers tend to be rather complex, to require special operating procedures, and to provide up to 12 analyses per hour rather than a truly continuous measurement. Other analyzers use a catalytic process to separate CH_4 by oxidizing all hydrocarbons other than CH_4 in a special controlled-temperature oxidizer. They may be either dual channel, in which the TOC and CH_4 are measured simultaneously, or cyclic, in which TOC and CH_4 are measured alternately. In some analyzers, activated carbon is used to remove NMOC and the CH_4 determination is then made.

Continuous NMOC analyzers suffer from a number of inherent technical problems that limit the reproducibility of the data they provide. A primary problem is the necessity of subtracting two comparably-sized numbers to obtain a measure of the NMOC. Because the difference between the TOC and CH_4 measurements--i.e., NMOC--is usually considerably smaller than either of the individual TOC or CH_4 concentrations, small errors in the TOC or CH_4 measurements may become large percent errors in the NMOC difference. Furthermore, ambient TOC and CH_4 concentrations must be measured on broad, relatively insensitive ranges of the instrument to accommodate the frequent wide excursions of the TOC and CH_4 ambient concentrations.* Also, FIDs are sensitive to changes in operating conditions such as flow rates, temperature, burner

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* For example, NMOC instruments are usually set to measure full-scale concentrations of TOC of 10 ppm. If the TOC concentration were 5 ppm and the CH_4 concentration were 4 ppm, NMOC would be 1 ppm. Assuming a 10% error in the TOC measurement--0.5 ppm--would result in a 50% error--1 ± 0.5 ppm--in the NMOC computations.

cleanliness, etc., which may result in zero and span drift. These characteristics make careful calibration and accurate balance of the TOC and CH_4 channels difficult.

Other NMOC analyzer problems over which the operator may have little or no control include measurement of TOC and CH_4 in different samples of air due to sequential, cyclic operation (usually not a problem for hourly averages), nonuniform sensitivity to various organic compounds and from one analyzer design to another, operational complexity, and potential safety hazards from hydrogen gas, which all FIDs require.

Experience to date with NMOC analyzers has not been encouraging. In the EPA document, Guidance for Collection of Ambient Non-Methane Organic Compound (NMOC) Data for Use in 1982 Ozone SIP Development, and Network Design and Siting Criteria for the NMOC and NO_2 Monitors,* it is noted that:

> Recent studies with commercial non-methane hydrocarbon (NMHC) analyzers have established the fact that these instruments yield unreliable data. Not only do instruments from different manufacturers produce different results, even instruments from the same manufacturer, with supposedly the same characteristics, yield data sometimes differing by a factor of two. (For comparison, measurements made with different SO_2 instruments have a correlation coefficient of better than 0.85). These studies were carried out by EPA laboratories as well as contractors, and the results are thus thought to be conclusive.

The overall sense of EPA-450/4-80-011 supports the use of FIDs in monitoring NMOC; however, this passage has been included here to emphasize the need for properly maintaining and calibrating these instruments. Experience at Systems Applications in the utilization of NMOC data for atmospheric simulations (including urban airshed modeling) underscores the expressed concerns in the quoted passage. Although some NMOC analyzers, particularly those based on chromatograhic separation, seem to give reasonable estimates of NMOC concentrations in some available data sets, the complexity of operation tends to make data from these instruments unreliable. Other methodologies, particularly those that involve activated charcoal adsorbtion, appear to give strong biases, and are not recommended.

A good example of the errors that can arise when NMOC analyzer data is used is found in Figure 4, which gives the NMOC and NO_x data for seven monitoring stations in the South Coast Air Basin (Los Angeles) area. The basin-wide average NMOC/NO_x value for the five years was about 3.5:1. The

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* EPA 450/4-80-011.

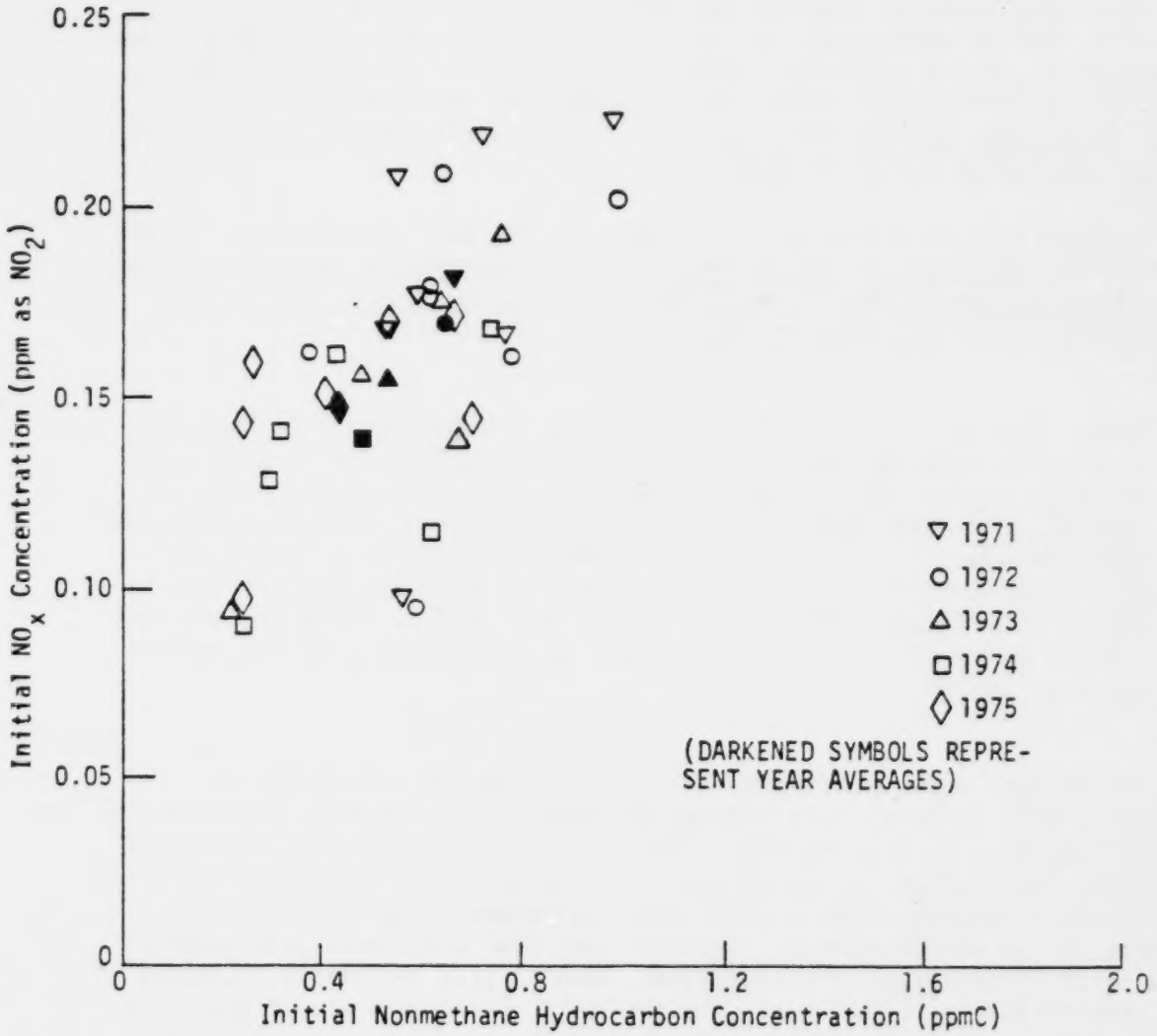

FIGURE 4. Los Angeles APCD data from seven monitoring stations for 1971 through 1975. (Source: Los Angeles APCD, 1971-1974; Southern California APCD, 1975)

emission inventory for the region, however, indicates a NMOC/NO_x ratio of greater than 5.0. All known atmospheric processes tend to reduce NO_x faster than NMOC. Therefore, the NMOC/NO_x ratio for the SOCAB should be greater than 5.

A similar discrepancy exists for data reported for the San Francisco Bay Area, for which the charcoal absorbtion methodology was also used to determine CH_4 and NMOC. De Mandel et al. (1979) reported 0600 to 0900 NMHC/NO_x ratios of 1.2 and 1.7 for San Francisco and San Jose, respectively, despite an emission ratio of 4.5.

Fortunately, a methodology exists for obtaining NMOC estimates directly from total hydrocarbon (THC) data. The THC-derived NMOC methodology is more robust than NMOC subtraction obtained from the instruments just described. Paskin and Kinosian (1974) first used the THC-derived NMOC technique in a study of hydrocarbon/NO_x/oxidant relationships in the Los Angeles basin. Unfortunately, this technique should be applied on a site-by-site basis.

Nonmethane hydrocarbon concentrations were calculated from measured THC concentrations using correlations derived from chromatographic data. Air samples were collected at stations in Los Angeles, Azusa, and Mira Loma between 0800 and 1000 during July, August, and September of 1971 (Bonamasa and Mayrsohn, 1971). Methane concentrations were subtracted from the THC concentrations to give the nonmethane hydrocarbon (NMHC ≈ NMOC) concentrations.

The reported THC-NMOC correlations were:

Station	THC-NMOC Correction
Los Angeles	NMOC = 0.64 (THC - 1.35)
Azusa	NMOC = 0.47 (THC - 1.4)
Mira Loma	NMOC = 0.73 (THC - 1.88)

A similar correlation was used by Killus et al. (1981) for the specification of initial conditions for the Urban Airshed Model:

$$NMHC = 0.8\ (THC - 1.4)$$

The data upon which the correlation was based were also for Los Angeles (Mayrsohn et al. 1975; 1976).

The regression intercept (the subtractor within the parenthesis) corresponds to the background of methane for the locality. The proportional term outside the parenthesis corresponds to the nonmethane fraction in urban

emissions. This proportionality can be determined from special gas chromatographic studies similar to those just noted. In the absence of such data, we recommend 0.7 as the NMOC emission fraction.

The local methane background can be obtained from THC data alone. Using a month of THC data (all hours), an average of the ten lowest THC concentrations provides a good estimate of the methane background. A small additional correction to this estimate can be performed by subtracting 0.03 ppmC from the average THC value as a correction for the natural background of NMOC (see Section 6).

When the THC-calculated NMOC methodology is used for Los Angeles, the result is much more realistic than for NMOC measured by subtraction devices. The difference between annual average NMOC concentrations is more than a factor of two; the ratio of calculated NMOC/NO_x by the THC methodology (Table 13) ranges from 7.19:1 to 8.58:1, values that are much more reasonable than those displayed in Figure 4. When the THC-derived NMOC data are used for San Francisco and San Jose*, calculated NMOC/NO_x ratios are 5:1 and 7.4:1 respectively, or four times the ratios reported by De Mandel et al. (1979).

Further confirmation of the THC-NMOC relationship can be seen in Table 14, which shows data obtained as part of an extensive monitoring program in Tulsa, Oklahoma. Two methods of NMOC measurement were used: a summation of individual hydrocarbon species obtained by chromatographic separation, and a Beckman 6800 NMOC monitor, a subtraction device that employs a chromatograhic adsorbent column for CH_4 separation. Data collected from these instruments are compared to NMOC calculated from the THC methodology just described.

For the instruments located at the Tulsa Post Office (Table 14a), all three methods for obtaining average NMOC concentrations gave identical results. For the health department site, however, the subtraction device yielded results significantly different from those obtained by chromatographic summation, while the THC-NMOC methodology was only 20 percent greater than the GC summation average.

EMISSIONS

As was previously described, the OZIPM/EKMA model is similar in concept to a Lagrangian photochemical dispersion model in that ozone and precursor concentrations within a well-mixed column of air are modeled as the column traverses the city. The column of well-mixed air is assumed to originate in

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* Based on maximum hourly averaged concentration for the month of September 1975, using the Los Angeles NMOC-THC relationship (Table 13).

TABLE 13. ANNUAL LOS ANGELES BASIN SEVEN-STATION MEAN NMOC AND NO_x FOR 0600-0900

Date	NO_x	Reported NMOC	Reported NMOC/NO_x	THC	Calculated NMOC*	Calculated NMOC/NO_x
1971	0.178	0.67	3.76	3.51	1.41	7.9
1972	0.167	0.65	3.89	3.51	1.41	8.45
1973	0.152	0.52	3.42	3.27	1.24	8.15
1974	0.139	0.47	3.38	3.11	1.19	8.58
1975	0.147	0.44	2.99	2.99	1.07	7.29

* NMOC = 0.7 (THC - 1.5)

TABLE 14. CDT AVERAGE NMHC AND NO_x AND RATIO OF NMHC TO NO_x

(a) Tulsa Post Office

Date	ΣNMHC* ppmC	Average 6-9 CDT NO_x, ppm	ΣNMHC / NO_x	NMHC** ppmC	NMHC / NO_x	THC ppmC	Calculated NMOC† ppmC	NMOC / NO_x
8/01	0.794	0.088	9.0	0.980	11.1	3.29	1.10	12.6
02	0.857	0.075	11.4	1.110	14.8	3.39	1.18	15.8
03	0.852	0.071	12.0	0.900	12.7	2.98	0.89	12.5
07	0.531	0.209	2.5	0.380	1.8	2.20	0.34	1.7
08	0.719	0.192	3.7	0.600	3.1	2.43	0.50	2.62
09	0.487	0.137	3.6	0.690	5.0	2.52	0.57	4.1
11	0.448	0.030	14.9	0.470	15.7	2.84	0.79	26.3
12	0.435	0.025	17.4	0.320	12.8	2.36	0.46	18.2
13	0.332	0.042	7.9	0.350	8.3	2.06	0.24	5.9
14	0.774	0.012	64.5	0.330	27.5	2.79	0.75	62.8
15	1.065	0.074	14.4	0.940	12.7	2.16	0.32	4.3
18	0.535	0.052	10.3	0.740	14.2	3.04	0.93	17.0
19	0.507	0.047	10.8	0.710	15.1	2.70	0.69	14.8
20	0.536	0.037	14.5	0.530	14.3	2.58	0.60	16.4
21	0.767	0.029	26.4	0.830	28.6	3.17	1.02	35.3
22	3.684	0.128	28.7	3.110	24.3	5.47	2.63	20.6
23	0.478	0.033	14.5	0.720	21.8	2.68	0.68	20.7
24	0.592	0.036	16.4	0.470	13.1	2.6	0.62	17.34
26	0.565	0.056	10.1	0.430	7.7	2.54	0.58	10.9
Mean	0.787	0.0723	10.9	0.77	10.7	2.80	0.778	10.8

* Measured by summation of individual compounds as determined by GC separation.

** Measured by Beckman 6800 NMHC monitor.

TABLE 14 (Concluded)

(b) Tulsa City/County Health Department

Date	NMHC ppmC	Average 6-9 CDT NO_x, ppm	NMHC / NO_x	NMHC ppmC	ΣNMHC / NO_x	THC ppmC	Calculated NMOC† ppmc	NMOC / NO_x
8/02	0.559	0.055	10.2	0.800	14.5	3.08	0.96	17.6
03	0.343	0.028	12.2	0.080	2.9	1.98	0.24	8.8
04	0.396	0.047	8.4	0.620	13.2	2.52	0.57	12.2
05	0.223	0.026	8.6	0.240	9.2	2.29	0.41	15.8
07	0.270	0.005	54.0	0.050	10.0	1.79	0.063	12.6
09	0.193	0.014	13.8	0.130	9.3	2.03	0.23	16.4
10	0.477	0.018	26.5	0.220	12.2	2.12	0.37	20.4
11	0.330	0.027	12.2	0.270	10.0	2.49	0.55	20.4
13	0.158	0.011	14.4	0.010	0.9	2.08	0.27	24.7
14	0.141	0.009	15.7	0.010	1.1	2.02	0.22	24.3
15	0.421	0.037	11.4	0.190	5.1	2.31	0.42	11.4
16	0.281	0.011	25.5	0.040	3.6	2.02	0.22	29.9
17	0.309	0.024	12.9	0.150	6.3	2.08	0.26	10.9
18	0.444	0.061	7.3	0.360	5.9	2.82	0.80	13.2
20	0.368	0.025	14.7	0.100	4.0	2.24	0.37	14.7
21	0.476	0.018	26.4	0.060	3.3	3.01	0.91	50.5
24	0.425	0.038	11.2	0.070	1.8	2.56	0.60	15.7
26	0.389	0.014	27.8	0.030	2.1	2.05	0.24	16.9
27	0.163	0.005	32.6	0.0	0.0	1.88	0.12	24.5
29	0.332	0.026	12.8	0.070	2.7	2.14	0.31	11.8
30	0.222	0.025	8.9	0.190	7.6	2.06	0.24	9.8
31	0.136	0.011	12.4	0.130	11.8	1.9	0.13	11.9
Mean	0.32	0.0243	13.2	0.17	7.15	2.26	0.39	15.9

† NMOC = 0.7 (THC - 1.7); The 1.7 ppmC methane background was obtained from the average of ten lowest hourly THC measurements: the methane background for the Health Department site was identical to that obtained for the Post Office site.

the urban core, and begin moving at 0800 LCT toward the site of the peak ozone concentration. Thus, the emissions occurring subsequent to 0800 LCT are determined by the track of the column. Within OZIPP, emissions data are input to the model for each hour after 0800 LCT, and are expressed relative to the initial concentrations. Thus, there are two basic and separate problems in deriving the necessary emission information:

(1) Determining emissions along the track of the theoretical column;

(2) Expressing the emissions derived in (1) relative to the initial concentrations. These initial concentrations are assumed to be the result of local urban emissions occurring prior to 0800.

Emission inventory data preparation is discussed in "Guidelines for Use of City-Specific EKMA in Preparing Ozone SIPs" (EPA-450/4-80-027). We note one recommended modification to those guidelines: we recommend that the NO_x emissions from large, elevated, point sources of NO_x be excluded from the emission inventory when performing EKMA simulations. To some extent, the questions of the degree of size and elevation need to be considered. The obvious reason for the exclusion of such emissions is that they may not impact on the air parcel that contains the maximum observed ozone value. Typically, some local knowledge of mixing height, wind direction aloft, and stack height can be applied to make sensible exclusions. The need for such exclusions arises from the major and erroneous effect large NO_x values might have on the EKMA model.

Numerous calculations using large-scale grid models seem to indicate that episodic ozone formation is insensitive to large point source emissions of NO_x. This seems to be because the relatively narrow horizontal spread and extreme vertical dispersion of concentrated NO_x plumes render them unlikely to impact a single ground monitoring site. Moreover, the well-known suppression of ozone by NO_x suggests that the highest measured ozone in an area is unlikely to be at a site of plume impingement. In any case, specific point source impacts should be assessed with a suitable plume model rather than with OZIPM/EKMA.

The approach recommended for computing emission fractions is one in which the initial emission density is related to initial conditions. The initial emission density is calculated as the emission density necessary to generate the initial concentrations observed within the column in one hour. If an initially empty column were "exposed" to the calculated initial emission density for one hour, the concentrations of precursors in the column at the end of the hour would equal the observed initial level. The emission density for any hour after 0800 LCT can then be related to the initial concentrations by means of the initial emission density. The emission fraction can therefore be calculated using the following equations:

$$Q_o = \alpha\, C_o H_o \quad , \tag{5-1}$$

and

$$E_i = \frac{Q_i}{Q_o} \quad , \tag{5-2}$$

where

Q_o = calculated initial emission density (kg/km^2)

C_o = initial precursor concentration (ppm)

H_o = initial mixing height (kilometers)

Q_i = emission density for hour i from the sequence of emissions (kg/km^2)

E_i = emission fraction for hour i

α = conversion factor for converting from volumetric to mass units (1.4 for NMOC; 0.49 for NO_x)

The factors Q_i and C_o are determined from external data, the countywide emissions density and initial concentrations of pollutants, respectively. The remaining three variables, Q_o, H_o, and E_i, are interdependent; specification of any one of these variables determines the others.

Since initial conditions in OZIPM may be related to the phenomenon of carryover, i.e., the percentage of the previous 24 hour's emissions remaining in the air column at 0800 hours, we may place some bounds on the factor E_i, at least for hydrocarbons. Because hydrocarbons decay very slowly at night, it is possible to estimate the mass of pollutants remaining in the air column from the previous night and day using mass balance calculations. Killus (1981) performed such a mass balance calculation for a high stagnation day in St. Louis, and estimated that carryover represented 35 percent of a day's emission of hydrocarbon. More extensive calculations involving the Urban Airshed Model (Killus et al., 1981) also yielded a 35 percent estimate for carryover.

The plausibility of the carryover of 35 percent of a day's hydrocarbon inventory may be seen in Figures 5 and 6. From Figure 5 one may see that, for Philadelphia, roughly 35 percent of a day's emissions of hydrocarbon and NO_x is emitted during the period of 1800-0800, i.e., during the evening, nighttime, and morning hours when winds are calm and the mixing layer is thin and

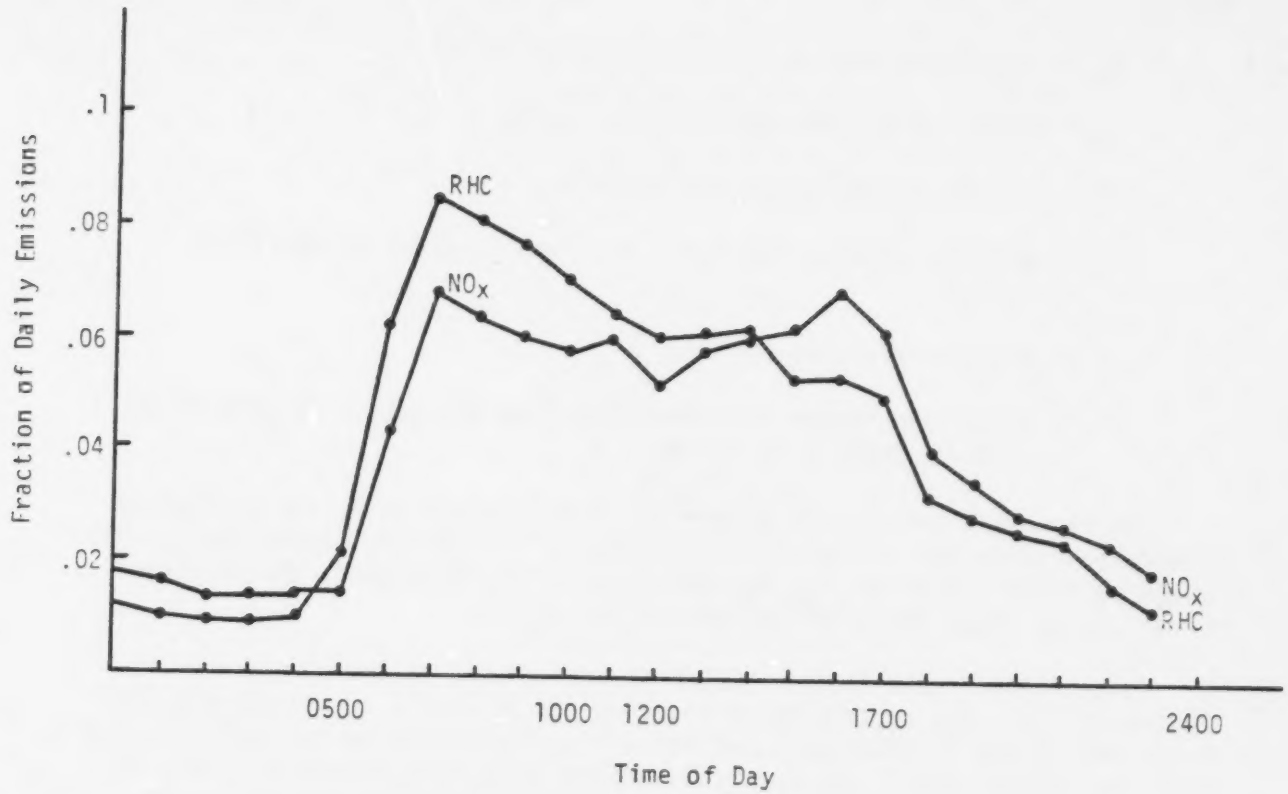

FIGURE 5. Diurnal variations of area source emissions in Philadelphia emissions inventory.

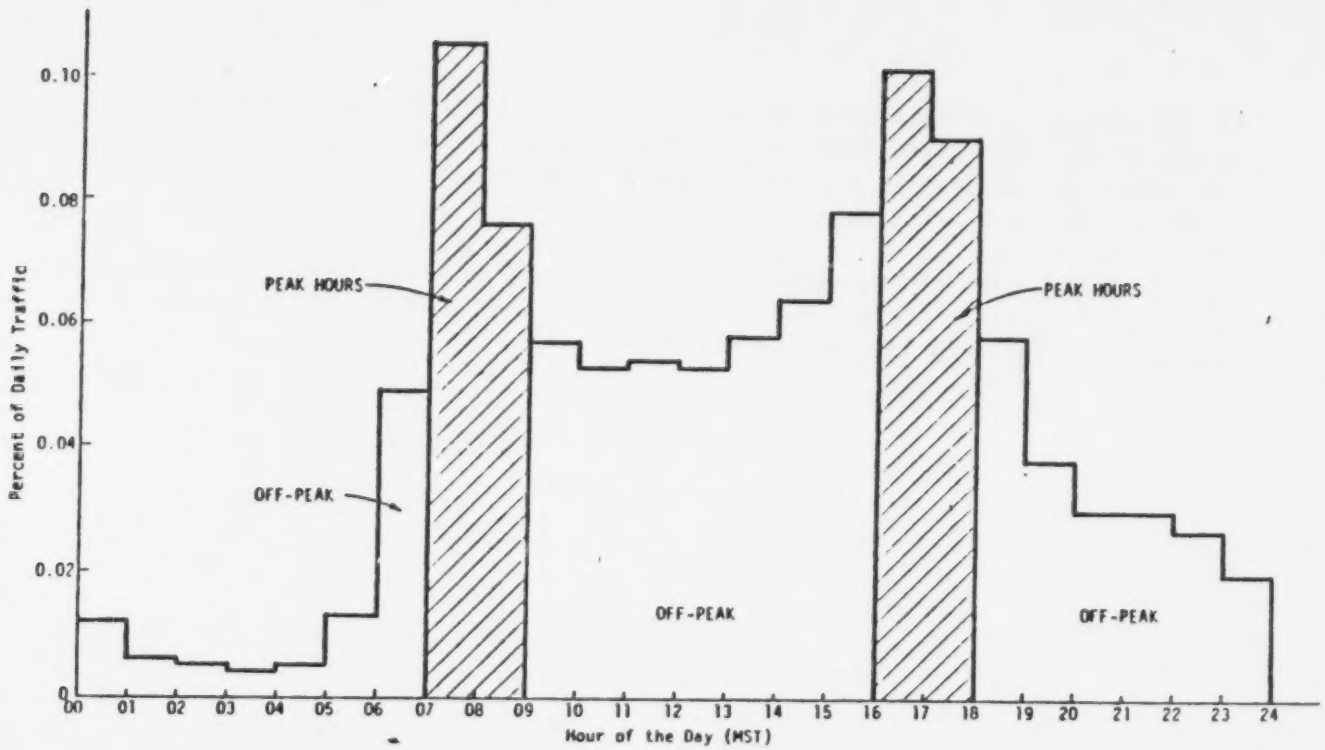

FIGURE 6. Diurnal variation in traffic flow in the Denver metropolitan area.

likely to trap pollutants. A similar fraction may be derived for Denver (Figure 6) based on diurnal traffic flow.

Since, at most, one third of a day's NMOC emissions may be represented in the pre-0800 column of air, and two-thirds of the day's emissions must occur during the simulation,

$$\sum_{i=1}^{10} E_i > 2.0 \quad ,$$

or the average E_i should be greater than 0.2. This limits the allowable height of the 0800 mixed layer (H_o). Thus, the morning mixing depth should not exceed 250 meters* in any case. However, it should also be low enough to allow an average E_i of greater than 0.2.

Note also that diurnal emission profiles such as those found in Figures 5 and 6 may be used to correct the daily averaged source emissions to hourly values, provided such information exists.

* EPA-450/4-80-027.

SECTION 6

BACKGROUND OZONE AND ITS PRECURSORS

The photochemical modeling of polluted atmospheres requires some estimation of what constitutes a "clean atmosphere." Boundary conditions for an urban Airshed Model, for example, should generally be specified as "clean air" concentrations to avoid driving the model with unknown source material. When clean air boundaries cannot be used, as for example when long-range transport of pollutants is a factor, control strategy calculations become more difficult, since projections of changes in long-range transport involve greater uncertainties than projections for a single urban area.

Conceptually, pollutant background must be divided into three components: tropospheric background, (biogenic and geogenic in origin) and background due to transport of anthropogenic precursors. Operationally, for control strategy calculations, the background must be divided into controllable and uncontrollable components. Clearly, the tropospheric and natural continental background is uncontrollable; in OZIPM/EKMA this background must be specified as transported (TRANS) or ALOFT pollutants or in the kinetic mechanism itself. Some fraction of anthropogenic background is controllable and appears in the initial conditions for the model. This portion will be rolled back with the emission control scenario.

OZONE AND NO_x

The estimation of background concentrations of ozone and nitrogen oxides can be made fairly easily. Ozone in remote areas has been measured in the range of 20-60 ppb, with occasional exceptions due to photochemical destruction or generation (Routhier et al., 1980), or from stratospheric intrusion (Singh et al., 1980). Nitrogen oxide data for clean atmospheres ranges from a few ppb to less than a tenth of a ppb (Kelly et al., 1980; Noxon, Norton, and Marovich, 1980). Clearly, background concentrations of NO_x are very small when compared with concentrations found in polluted atmospheres. Therefore, background NO_x does not constitute a major perturbation in the urban photochemical system. For example, a concentration of 3 ppb NO_x will generate only about 10 ppb of ozone before conversion to nitric acid.

We recommend the use of a natural background of 40 ppb (0.04 ppm) ozone and 1 ppb (0.001 ppm) NO_x. These concentrations should be specified on TRANS card inputs to OZIPM.

REACTIVITY OF THE FREE TROPOSPHERE

The reactivity of unpolluted air is difficult to estimate, because it is the result of a great many compounds, each having a low concentration, whose sum effect is nevertheless of significance to the smog process.* For the purposes of this discussion, the term "reactivity" is best defined in a specific chemical sense as the rate at which hydroxyl radicals react with atmospheric gases to form peroxyl radicals:

$$OH + HC \rightarrow RO_2 \quad .$$

Whitten, Killus, and Johnson (1983) performed an extensive review of background reactivity phenomena and recommended three estimates of ROG concentrations, speciation, and OH-to-RO_2 conversion rates (see Table 15). Presumably, the low, mid, and high background estimates correspond respectively to tropospheric, continental, and anthropogenic transport background.

Singh and Sales (1982) reported measurements of methane and light alkanes over the eastern Pacific (Table 16 and Seiler (1974) reported background concentrations of CO (Figure 7). Using these data, we can calculate the hydrocarbon and CO/OH-to-RO_2 conversion reactivity directly, and can use photochemical mechanisms to estimate the equilibrium concentration of carbonyls. We arrive at an OH-to-RO_2 conversion rate of 94 ppm^{-1} min^{-1} plus 2

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* These peroxyl radicals (HO_2, CH_3O_2, CH_3CO_3, etc.) are responsible for conversion of NO to NO_2 in the photochemical process of smog formation that eventually yields ozone. This definition of reactivity is not always suitable for the background effect because it makes no special distinction for variations in concentration levels. A high concentration of slowly reacting species can have the same "reactivity" as a low concentration of quickly reacting species. However, the latter can only be associated with fresh emissions because any true background mixture must be relatively stable in both overall concentration and speciation character.

TABLE 15. BACKGROUND OF REACTIVE HYDROCARBONS. (Source: Whitten, Killus, and Johnson, 1983).

Carbon Fraction		Concentration	Species	
Low	0.91	0.03 ppmC	PAR	0.03 ppmC
	0.09	0.003 ppm	CARB	
		0.1 ppm	CO	OH to RO_2 reactivity = 125 min^{-1}
Mid	0.61	0.035 ppmC	PAR	0.043 ppmC
	0.083	0.0008 ppm	ARO	(+ 0.015 ppm CARB)
	0.034	0.001 ppm	ETH	
	0.014	0.0004 ppm	OLE	
	0.26	0.015 ppm	CARB	OH to RO_2 reactivity
	0.0005	0.00003 ppm	DCRB	
		0.2 ppm	CO	= 387 min^{-1}
High	0.57	0.1 ppmC	PAR	0.144 ppmC
	0.07	0.002 ppm	ARO	(+ 0.03 ppm CARB)
	0.12	0.01 ppm	ETH	
	0.07	0.006 ppm	OLE	
	0.17	0.03 ppm	CARB	
	0.0005	0.00008 ppm	DCRB	OH to RO_2 reactivity
		0.5 ppm	CO	1153 min^{-1}

Note: All estimates include 0.015 ppmC PAR as surrogate for background methane.

TABLE 16. Average light hydrocarbon concentrations measured over the eastern Pacific.

Latitude	Longitude (°W)	Concentration* (ppb)									
		CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$i\text{-}C_5H_{12}$	$n\text{-}C_5H_{12}$
40-30°N	124-117	1664	2.37	0.12	0.46	0.80	0.05	0.21	0.51	0.24	0.42
30-20°N	117-108	1639	1.84	0.10	0.42	0.72	0.18	0.20	0.66	0.30	0.43
20-10°N	108-97	1601	0.94	0.05	0.37	0.39	0.30	0.28	0.65	0.24	0.37
10-0°N	97-89	1557	0.34	0.11	0.09	0.27	0.16	0.10	0.30	0.15	0.26
0-10°S	89-79	1520	0.29	0.07	0.16	0.11	0.15	0.13	0.19	0.18	0.29
10-20°S	79-75	1531	0.27	0.07	0.33	0.20	0.28	0.11	0.13	0.20	0.36
20-32°S	75-72	1526	0.23	0.08	0.13	0.11	0.07	0.06	0.14	0.05	0.17

*Typically based on an average of 2 to 5 samples collected over the 10° latitude belt. Data collected during 30 Nov. to 21 Dec. 1981.

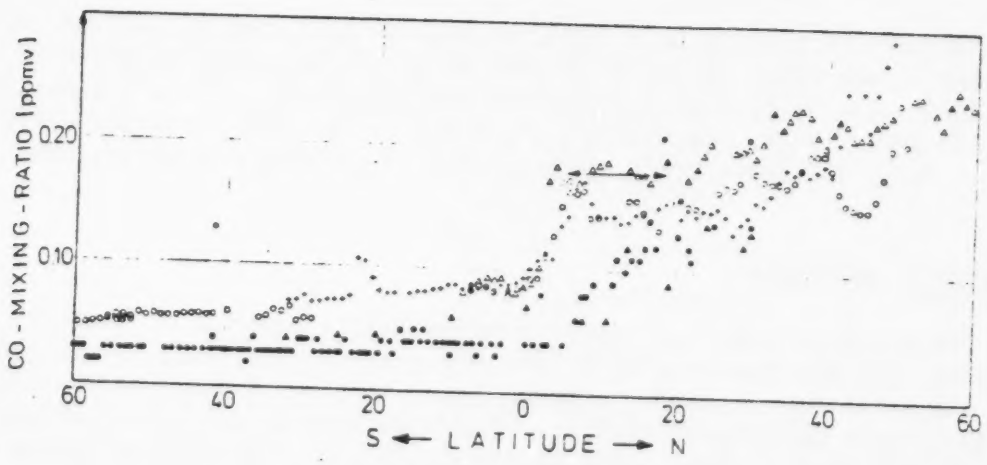

FIGURE 7. CO-mixing ratios in marine air masses over the Atlantic and Pacific oceans. Full triangles represent the *Eltanin*-cruise No. 31 (1967) from San Francisco to New Zealand (Robinson & Robbins, 1969). The open triangles represent the GARP-expedition in 1969 from 10° S to 60° N along 30° W (Seiler & Junge, 1970) over the Atlantic ocean; the solid lines represent the average CO-mixing ratio found by Ripperton et al. (1972) in the Bomex-area over the Atlantic ocean; the open circles represent the "Shackleton" expedition in November 1971 over the Atlantic ocean; the crosses represent the "Shackleton" expedition in April 1972 over the Atlantic ocean and the points represent the cruise from the USA to the Antarctic (Swinnerton et al., 1973) over the Pacific ocean.

ppb of carbonyls, mostly formaldehyde.* The overall OH to RO_2 reactivity including carbonyls is 129 min^{-1}, in good agreement with the estimates of Whitten, Killus, and Johnson (1983).

Because the tropospheric background concentrations of methane and light hydrocarbons are nearly invariant, it is possible to account for their effect as part of the kinetic mechanism itself. The conversion of hydroxyl to peroxyl radicals may be modeled as two pseudo first-order reactions:

$$OH \xrightarrow{(+CH_4 + ROG)} MeO_2 \qquad 28\ min^{-1} \qquad (6\text{-}1)$$

$$OH \xrightarrow{+ CO} HO_2 \qquad 66\ min^{-1} \qquad (6\text{-}2)$$

The tropospheric background of CARB, because CARB is highly reactive, must be included in the TRANS inputs to OZIPM. As the initial concentration of CARB (or "HCHO"--see Section 4) is destroyed photochemically, it is replenished by the CARB generated by reaction 6-1 (followed by reaction 30 in the CBM-III/EKMA). Thus, the equilibrium concentration of carbonyls is maintained.

CONTINENTAL BACKGROUND

The boundary layer over continents receives a variety of biogenic, geogenic, and anthropogenic emissions that constitute a reactive background over and above the tropospheric background. Whitten, Killus, and Johnson (1983) noted a very high percentage of unidentified compounds in various measurements of rural air. This is not surprising. Biogenic emissions are known to include isoprene, terpenes, heavy paraffins (plant waxes), ethene (a fruit hormone), esters, and alcohols, among others. Geogenic emissions from natural gas and petroleum seepage, can mimic anthropogenic emissions (many of which are, after all, derived from petroleum).

The mid and background estimates in Table 15 should be taken as representative of the minimum continental background; the high estimates may be taken as associated with a substantial amount of urban transport. The high should not be used for OZIPM boundary conditions (TRANS) unless the transported precursors are deemed "uncontrollable", i.e., if future controls are unlikely to affect the upwind anthropogenic emission areas.

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* Kinetic theory predicts an additional 2 ppb of acetone from light alkane oxidation. However, acetone is much less reactive than other carbonyl compounds and we have not included it in the background CARB.

Atmospheric measurements indicate that the reactive background decreases with height. The data of Grosjean et al. (1981), for example, indicate a gradual decrease in concentrations until the tropospheric background is approached at 300 to 500 m. The total mass loading of continental background hydrocarbons can be represented by the mid-range background estimate taken as a constant concentration up to 250 m. The concentration should be inversely proportional to mixing height; e.g., if the initial mixing depth is taken to be 100 m, all background concentrations should be multiplied by 2.5.

To make the mid-range background estimate consistent with our previous methodology for treating tropospheric background (Equations 6-1 and 6-2), we made the following changes to the mid-range estimate. The 0.015 PAR surrogate is subtracted from the PAR category. The rate constant for Reaction 6 is increased to 88 min^{-1} to account for 0.2 ppm CO. Also, the 0.015 ppm CARB in the mid-range estimate of Whitten, Killus, and Johnson includes 0.005 ppm acetone. Since we are neglecting acetone in our background reactivity estimates (acetone having been shown to be relatively unreactive), we reduce the CARB concentration to 0.01. Thus, the following concentrations (ppm) should be input to OZIPM as TRANS

	Fraction	Concentration (ppm)	Species
	0.5305	0.02	PAR
	0.1273	0.0008	ARO (0.0048 ppmC)
	0.05310	0.001	ETH (0.002 ppmC)
	0.0212	0.0004	OLE (0.0008 ppmC)
	0.2652	0.01	CARB
	0.0027	0.00003	DCRB (0.0001 ppmc)
Total	0.0377		

Reactions to account for tropospheric background are

$$OH + MeO_2 \quad 28\ min^{-1} \quad ,$$

$$OH + HO_2 \quad 88\ min^{-1} \quad .$$

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Appendix A

Recommended Rates for Carbon-Bond Mechanism-III/EKMA in OZIPM

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
1	$NO_2 \rightarrow NO + O$	1.0*	0
2	$O + (O_2) + (M) \rightarrow O_3$	4.40×10^{6}**	0
3	$NO + O_3 \rightarrow NO_2 + O_2$	26.6	1450
4	$NO_2 + O_3 \rightarrow NO_3 + O_2$	0.048	2450
5	$NO_2 + O \rightarrow NO + O_2$	1.3×10^{4}	0
6	$OH + O_3 \rightarrow HO_2 + O_2$	100	1000
7	$HO_2 + O_3 \rightarrow OH + 2O_2$	2.40	1525
8	$OH + NO_2 \rightarrow HNO_3$	1.60×10^{4}	0
9	$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	440	0
10	$NO + NO + (O_2) \rightarrow NO_2 + NO_2$	1.50×10^{-4}	0
11	$NO + NO_3 \rightarrow NO_2 + NO_2$	2.80×10^{4}	0
12	$NO_2 + NO_3 + H_2O \rightarrow 2HNO_3$	1.3×10^{-3}†	-1.06×10^{4}
13	$NO + HO_2 \rightarrow NO_2 + OH$	1.20×10^{4}	0
14	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.50×10^{4}	0
15	$X + PAR \rightarrow$	10^{5}	0
16	$OH + PAR \xrightarrow{O_2} MEO_2 + H_2O$	1200	560
17	$O + OLE \xrightarrow{O_2} MEO_2 + ACO_3 + X$	2700	325
18	$O + OLE \rightarrow HCHO + PAR$	2700	325
19	$OH + OLE \xrightarrow{O_2} RAO_2$	3.70×10^{4}	-540

Continued

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
20	O_3 + OLE → HCHO + CRIG	0.008	1900
21	O_3 + OLE → HCHO + MCRG + X	0.008	1900
22	$O + ETH \xrightarrow{O_2} MEO_2 + HO_2 + CO$	600	800
23	O + ETH → HCHO + PAR	600	800
24	$OH + ETH \xrightarrow{O_2} RBO_2$	1.20×10^4	-382
25	O_3 + ETH → HCHO + CRIG	0.0024	2560
26	$NO + ACO_3 \xrightarrow{O_2} NO_2 + MEO_2$	1.04×10^4	0
27	$NO + RBO_2 \xrightarrow{O_2} NO_2$ + HCHO + HO_2 + HCHO	1.20×10^4	0
28	$NO + RAO_2 \xrightarrow{O_2} NO_2$ + HCHO + HO_2 + HCHO	1.20×10^4	0
29	$NO + MEO_2 \xrightarrow{O_2} NO_2$ + HCHO + MEO_2 + X	3700	0
30	$NO + MEO_2 \xrightarrow{O_2} NO_2$ + HCHO + HO_2	7400	0
31	$NO + MEO_2$ → NRAT	900	0
32	RBO_2 → HCHO + HCHO + HO_2 + O_2	5.0	0
33	RAO_2 → HCHO + HCHO + HO_2 + O_2	20	0
34	OH + HCHO → CRO_2 + X	100	0
35	$OH + HCHO \xrightarrow{O_2} HO_2 + CO$	9000	0
36	$OH + HCHO \xrightarrow{O_2} ACO_3$ + X	8200	0
37	HCHO → CO + H_2	(0.24)*	0
38a	$HCHO + \xrightarrow{O_2}$ QQ	(0.564)*	0
38b	$QQ \xrightarrow{2\ O_2} HO_2 + HO_2 + CO$	8867	
38c	QQ → MEO_2 + MEO_2 + X + XCO	1133	
38d	XCO → X + CO	10^4	

Continued

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
39	$NO_2 + ACO_3 \rightarrow PAN$	7000	0
40	$PAN \rightarrow ACO_3 + NO_2$	0.022	1.35×10^4
41	$HO_2 + ACO_3 \rightarrow$ Stable products	1.50×10^4	0
42	$HO_2 + MEO_2 \rightarrow$ Stable products	9000	0
43	$NO + CRIG \rightarrow NO_2 + HCHO$	1.20×10^4	0
44	$NO_2 + CRIG \rightarrow NO_3 + HCHO$	8000	0
45	$HCHO + CRIG \rightarrow$ Ozonide	2000	0
46	$NO + MCRG \rightarrow NO_2 + HCHO + PAR$	1.20×10^4	0
47	$NO_2 + MCRG \rightarrow NO_3 + HCHO + PAR$	8000	0
48	$HCHO + MCRG \rightarrow$ Ozonide	2000	0
49	$CRIG \rightarrow CO + H_2O$	670**	0
50	$CRIG \rightarrow$ Stable products	240**	0
51	$CRIG \xrightarrow{O_2} HO_2 + HO_2 + CO$	90**	0
52	$MCRG \rightarrow$ Stable products	150**	0
53	$MCRG \xrightarrow{O_2} MEO_2 + OH + CO$	340**	0
54	$MCRG \xrightarrow{O_2} MEO_2 + HO_2$	425**	0
55	$MCRG \xrightarrow{O_2} HCHO + HO_2 + CO + HO_2$	85**	0
56	$OH + ARO \xrightarrow{O_2} RARO + H_2O$	6000	600
57	$OH + ARO \xrightarrow{O_2} HO_2 + OPEN$	1.45×10^4	400
58	$NO + RARO \xrightarrow{O_2} NO_2 + PHEN + HO_2$	4000	0

Continued

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
59	$OPEN + NO \xrightarrow{O_2} NO_2 + DCRB + X + APRC$	6000	0
60	$APRC \xrightarrow{O_2} DCRB + HCHO + CO + X$	10^{4**}	0
61	$APRC \xrightarrow{O_2} HCHO + HCHO + CO + CO$	10^{4**}	0
62	$PHEN + NO_3 \rightarrow PHO + HNO_3$	5000	0
63	$PHO + NO_2 \rightarrow NPHN$	4000	0
64	$PHO + HO_2 \rightarrow PHEN$	5.00×10^4	0
65	$OPEN + O_3 \rightarrow DCRB + X + APRC$	40	0
66	$OH + PHEN \xrightarrow{O_2} HO_2 + APRC + PAR + HCHO$	3.00×10^4	0
67	$DCRB \xrightarrow{O_2} HO_2 + ACO_3 + CO$	$(0.02 \times K_1)^{**}$	0
68	$PHEN + OH \rightarrow PHO$	10^4	0
69	$CRO_2 + NO \xrightarrow{O_2} NO_2 + HCHO + ACO_3 + X$	1.20×10^4	0
70	$DCRB + OH \rightarrow ACO_3 + CO$	25000.	0
71	$HONO \rightarrow OH + NO$	$(3.1^{*}$ or $0.18^{**} \times K_1)$	0
72	$OH + NO \rightarrow HONO$	9770	0
73	$O_3 \rightarrow O^1D$	$(0.53)^{*}$	0
74	$O^1D \xrightarrow{+(M)} O$	4.44×10^{10}	0
75	$O^1D + H_2O \rightarrow OH + OH$	3.4×10^5	0
76	$O_3 \rightarrow O$	$(1.0)^{*}$	
77	$NR \rightarrow$	0.0	

* Sunlight-dependent; rate constant is correction factor for OZIPM input, units of min^{-1}.

† Units of $ppm^{-2}min^{-1}$.

** Units of min^{-1}.

Appendix B

BOND GROUPS PER MOLECULE

TABLE B-1. Molecular Weights of Molecules
(in Alphabetical Order)

Species No.	SAROAD Code	Chemical Name	Molecular Weight
1	43814	1,1,1-TRICHLOROETHANE	133.42
2	43820	1,1,2-TRICHLOROETHANE	131.66
3	43813	1,1-DICHLOROETHANE	98.97
4	45225	1,2,3-TRIMETHYLBENZENE	120.19
5	45208	1,2,4-TRIMETHYLBENZENE	120.19
6	45207	1,3,5-TRIMETHYLBENZENE	120.19
7	43218	1,3-BUTADIENE	54.09
8	46201	1,4-DIOXANE	88.12
9	43245	1-HEXENE	84.16
10	43224	1-PENTENE	70.13
11	43312	1-T-2-C-4-TM-CYCLOPENTANE	112.23
12	43296	2,2,3-TRIMETHYLPENTANE	114.23
13	43276	2,2,4-TRIMETHYLPENTANE	114.22
14	43299	2,2,5-TRIMETHYLPENTANE	114.23
15	43291	2,2-DIMETHYLBUTANE	86.17
16	43280	2,3,3-TRIMETHYLPENTANE	114.22
17	43279	2,3,4-TRIMETHYLPENTANE	114.22
18	43234	2,3-DIMETHYL-1-BUTENE	84.16
19	50001	2,3-DIMETHYLBUTANE	86.17
20	43274	2,3-DIMETHYLPENTANE	100.20
21	43277	2,4-DIMETHYLHEXANE	114.22
22	43271	2,4-DIMETHYLPENTANE	100.20
23	43278	2,5-DIMETHYLHEXANE	114.22
24	43308	2-BUTYLETHANOL	118.17
25	43311	2-ETHOXYETHANOL	90.12
26	43452	2-ETHOXYETHYL ACETATE	132.00
27	50002	2-ETHYL-1-BUTENE	84.16
28	43310	2-METHOXYETHANOL	76.09
29	43229	2-METHYL PENTANE	86.17
30	43225	2-METHYL-1-BUTENE	70.13
31	43228	2-METHYL-2-BUTENE	70.13
32	50004	2-METHYL-2-PENTENE	84.16
33	43275	2-METHYLHEXANE	100.20
34	43230	3-METHYL PENTANE	86.17
35	43223	3-METHYL-1-BUTENE	70.13
36	43211	3-METHYL-1-PENTENE	84.16
37	43270	3-METHYL-T-2-PENTENE	84.16
38	43298	3-METHYLHEPTANE	114.23
39	43295	3-METHYLHEXANE	100.20
40	43293	4-METHYL-T-2-PENTENE	84.16

TABLE B-1. (Continued)

Species No.	SAROAD Code	Chemical Name	Molecular Weight
41	43297	4-METHYLHEPTANE	114.23
42	45221	A-METHYLSTYRENE	118.15
43	50025	A-PINENE	136.24
44	43503	ACETALDEHYDE	44.05
45	43404	ACETIC ACID	60.05
46	43551	ACETONE	58.08
47	43702	ACETONITRILE	41.05
48	43206	ACETYLENE	26.04
49	43704	ACRYLONITRILE	53.06
50	50015	ANTHRACENE	178.22
51	50020	B-METHYLSTYRENE	118.15
52	50026	B-PINENE	136.24
53	45201	BENZENE	78.11
54	50024	BENZYLCHLORIDE	112.56
55	43213	BUTENE	56.10
56	43510	BUTYRALDEHYDE	72.12
57	50003	C-3-HEXENE	84.16
58	43115	C-7 CYCLOPARAFFINS	98.19
59	43116	C-8 CYCLOPARAFFINS	112.23
60	43117	C-9 CYCLOPARAFFINS	126.26
61	43511	C3 ALDEHYDE	58.08
62	43512	C5 ALDEHYDE	86.14
63	43289	C6 OLEFINS	84.16
64	43294	C7-OLEFINS	98.18
65	43513	C8 ALDEHYDE	128.21
66	43290	C8 OLEFINS	112.23
67	43807	CARBON TETRABROMIDE	331.67
68	43804	CARBON TETRACHLORIDE	153.84
69	43443	CELLOSOLVE ACETATE	132.00
70	43803	CHLOROFORM	119.39
71	43217	CIS-2-BUTENE	56.10
72	43227	CIS-2-PENTENE	70.13
73	50019	CRYOFLOURANE (FREON 114)	170.93
74	43248	CYCLOHEXANE	84.16
75	43264	CYCLOHEXANONE	98.15
76	43273	CYCLOHEXENE	82.14
77	43242	CYCLOPENTANE	70.14
78	43292	CYCLOPENTENE	68.11
79	43207	CYCLOPROPANE	42.08
80	50027	D-LIMONENE	136.24

TABLE B-1. (Continued)

Species No.	SAROAD Code	Chemical Name	Molecular Weight
81	43320	DIACETONE ALCOHOL	116.16
82	43823	DICHLORODIFLUOROMETHANE	120.91
83	43802	DICHLOROMETHANE	84.94
84	50018	DIMETHYL ETHER	46.07
85	43450	DIMETHYL FORMAMIDE	73.09
86	50017	DIMETHYL-2,3,DIHYDRO-1H-INDENE	146.23
87	45103	DIMETHYLETHYLBENZENE	134.21
88	50012	DIMETHYLNAPHTHALENE	156.22
89	43287	DOCOSANE	310.59
90	43285	EICOSANE	282.54
91	43202	ETHANE	30.07
92	43433	ETHYL ACETATE	88.10
93	43438	ETHYL ACRYLATE	100.11
94	43302	ETHYL ALCOHOL	46.07
95	43812	ETHYL CHLORIDE	64.52
96	43351	ETHYL ETHER	74.12
97	43219	ETHYLACETYLENE	54.09
98	43721	ETHYLAMINE	45.09
99	45203	ETHYLBENZENE	106.16
100	43288	ETHYLCYCLOHEXANE	112.23
101	43203	ETHYLENE	28.05
102	43815	ETHYLENE DICHLORIDE	99.00
103	43370	ETHYLENE GLYCOL	62.07
104	43601	ETHYLENE OXIDE	44.05
105	50011	ETHYLNAPHTHALENE	156.22
106	43502	FORMALDEHYDE	30.03
107	43368	GLYCOL	62.07
108	43367	GLYCOL ETHER	62.07
109	43286	HENEICOSANE	296.57
110	43282	HEPTADECANE	240.46
111	43232	HEPTANE	100.20
112	50005	HEPTENE	98.18
113	43281	HEXADECANE	226.44
114	43231	HEXANE	86.17
115	43214	ISO-BUTANE	58.12
116	43306	ISO-BUTYL ALCOHOL	74.12
117	43304	ISO-PROPYL ALCOHOL	60.09
118	43446	ISOBUTYL ACETATE	116.16
119	43451	ISOBUTYL ISOBUTYRATE	144.21
120	43215	ISOBUTYLENE	56.10

TABLE B-1. (Continued)

Species No.	SAROAD Code	Chemical Name	Molecular Weight
121	43120	ISOMERS OF BUTENE	56.10
122	45105	ISOMERS OF BUTYLBENZENE	134.21
123	43109	ISOMERS OF DECANE	142.28
124	45106	ISOMERS OF DIETHYLBENZENE	134.21
125	43112	ISOMERS OF DODECANE	170.33
126	45104	ISOMERS OF ETHYLTOLUENE	120.19
127	43106	ISOMERS OF HEPTANE	100.20
128	43105	ISOMERS OF HEXANE	86.17
129	45234	ISOMERS OF METHYLPROP. BENZENE	134.21
130	43108	ISOMERS OF NONANE	128.25
131	43107	ISOMERS OF OCTANE	114.23
132	43114	ISOMERS OF PENTADECANE	212.41
133	43122	ISOMERS OF PENTANE	72.15
134	43121	ISOMERS OF PENTENE	70.13
135	45108	ISOMERS OF PROPYLBENZENE	120.19
136	43113	ISOMERS OF TETRADECANE	198.38
137	43111	ISOMERS OF TRIDECANE	184.36
138	45107	ISOMERS OF TRIMETHYLBENZENE	120.19
139	43110	ISOMERS OF UNDECANE	156.30
140	45102	ISOMERS OF XYLENE	106.16
141	43243	ISOPRENE	68.13
142	43444	ISOPROPYL ACETATE	104.00
143	43119	LACTOL SPIRITS	114.23
144	50022	M-CRESOL (3-METHYLBENZENOL)	110.16
145	45212	M-ETHYLTOLUENE	120.19
146	45205	M-XYLENE	106.16
147	43201	METHANE	16.04
148	43432	METHYL ACETATE	74.08
149	43301	METHYL ALCOHOL	32.04
150	43445	METHYL AMYL ACETATE	140.00
151	43801	METHYL CHLORIDE	50.49
152	43552	METHYL ETHYL KETONE	72.10
153	43560	METHYL ISOBUTYL KETONE	100.16
154	43559	METHYL N-BUTYL KETONE	100.16
155	43209	METHYLACETYLENE	40.06
156	50016	METHYLANTHRACENE	192.25
157	43261	METHYLCYCLOHEXANE	85.16
158	43262	METHYLCYCLOPENTANE	84.16
159	43272	METHYLCYCLOPENTENE	82.14
160	43819	METHYLENE BROMIDE	173.85

TABLE B-1. (Continued)

Species No.	SAROAD Code	Chemical Name	Molecular Weight
161	50010	METHYLNAPHTHALENE	142.19
162	43118	MINERAL SPIRITS	114.23
163	45801	MONOCHLOROBENZENE	112.56
164	43212	N-BUTANE	58.12
165	43435	N-BUTYL ACETATE	116.16
166	43305	N-BUTYL ALCOHOL	74.12
167	43238	N-DECANE	142.28
168	43255	N-DODECANE	170.33
169	43260	N-PENTADECANE	212.41
170	43220	N-PENTANE	72.15
171	43303	N-PROPYL ALCOHOL	60.09
172	45209	N-PROPYLBENZENE	120.19
173	43259	N-TETRADECANE	198.38
174	43258	N-TRIDECANE	184.36
175	45101	NAPHTHA	114.23
176	43284	NONADECANE	268.51
177	43235	NONANE	128.25
178	50021	O-CRESOL (2-METHYLBENZENOL)	110.16
179	45211	O-ETHYLTOLUENE	120.19
180	45204	O-XYLENE	106.16
181	43283	OCTADECANE	254.49
182	43233	OCTANE	114.23
183	43265	OCTENE	112.21
184	50023	P-CRESOL (4-METHYLBENZENOL)	110.16
185	45206	P-XYLENE	106.16
186	43817	PERCHLOROETHYLENE	165.85
187	45300	PHENOLS	94.11
188	50006	PROPADIENE	40.06
189	43204	PROPANE	44.09
190	43504	PROPRIONALDEHYDE	58.08
191	43434	PROPYL ACETATE	102.13
192	43205	PROPYLENE	42.08
193	43369	PROPYLENE GLYCOL	76.00
194	43602	PROPYLENE OXIDE	58.08
195	50013	PROPYLNAPHTHALENE	170.25
196	43208	PROPYNE	40.06
197	45216	SEC-BUTYLBENZENE	134.21
198	45220	STYRENE	104.14
199	43123	TERPENES	136.24
200	43309	TERT-BUTYL ALCOHOL	74.12

TABLE B-1. (Concluded)

Species No.	SAROAD Code	Chemical Name	Molecular Weight
201	45215	TERT-BUTYLBENZENE	134.21
202	43390	TETRAHYDROFURAN	72.10
203	45232	TETRAMETHYLBENZENE	134.21
204	45202	TOLUENE	92.13
205	43216	TRANS-2-BUTENE	56.10
206	43226	TRANS-2-PENTENE	70.13
207	45233	TRI/TETRAALKYL BENZENE	148.23
208	43824	TRICHLOROETHYLENE	131.40
209	43811	TRICHLOROFLOUROMETHANE	137.38
210	43821	TRICHLOROTRIFLOUROETHANE	187.38
211	43740	TRIMETHYL AMINE	59.11
212	43822	TRIMETHYLFLUOROSILANE	92.00
213	50014	TRIMETHYLNAPHTHALENE	170.25
214	43241	UNDECANE	156.30
215	43000	UNKNOWN SPECIES	86.00
216	43860	VINYL CHLORIDE	62.50
217	45401	XYLENE BASE ACIDS	230.00

TABLE B-2. BOND GROUPS PER MOLECULE
(IN ALPHABETICAL ORDER)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43814	1,1,1-TRICHLOROETHANE	-	-	-	-	-	2
43820	1,1,2-TRICHLOROETHANE	-	-	-	-	-	2
43813	1,1-DICHLOROETHANE	-	-	-	-	-	2
45225	1,2,3-TRIMETHYLBENZENE	-	3	1	-	-	-
45208	1,2,4-TRIMETHYLBENZENE	-	3	1	-	-	-
45207	1,3,5-TRIMETHYLBENZENE	-	3	1	-	-	-
43218	1,3-BUTADIENE	2	-	-	-	-	-
46201	1,4-DIOXANE	1	2	-	2	-	-
43245	1-HEXENE	1	4	-	-	-	-
43224	1-PENTENE	1	3	-	-	-	-
43312	1-T-2-C-4-TM-CYCLOPENTANE	-	8	-	-	-	-
43296	2,2,3-TRIMETHYLPENTANE	-	8	-	-	-	-
43276	2,2,4-TRIMETHYLPENTANE	-	8	-	-	-	-
43299	2,2,5-TRIMETHYLPENTANE	-	8	-	-	-	-
43291	2,2-DIMETHYLBUTANE	-	6	-	-	-	-
43280	2,3,3-TRIMETHYLPENTANE	-	8	-	-	-	-
43279	2,3,4-TRIMETHYLPENTANE	-	8	-	-	-	-
43234	2,3-DIMETHYL-1-BUTENE	1	4	-	-	-	-
50001	2,3-DIMETHYLBUTANE	-	6	-	-	-	-
43274	2,3-DIMETHYLPENTANE	-	7	-	-	-	-
43277	2,4-DIMETHYLHEXANE	-	8	-	-	-	-
43271	2,4-DIMETHYLPENTANE	-	7	-	-	-	-
43278	2,5-DIMETHYLHEXANE	-	8	-	-	-	-
43308	2-BUTYLETHANOL	-	5	-	1	-	-
43311	2-ETHOXYETHANOL	-	3	-	1	-	-
43452	2-ETHOXYETHYL ACETATE	-	4	-	2	-	-
50002	2-ETHYL-1-BUTENE	1	4	-	-	-	-
43310	2-METHOXYETHANOL	-	2	-	1	-	-
43229	2-METHYL PENTANE	-	6	-	-	-	-
43225	2-METHYL-1-BUTENE	1	3	-	-	-	-
43228	2-METHYL-2-BUTENE	-	3	-	2	-	-
50004	2-METHYL-2-PENTENE	-	4	-	2	-	-
43275	2-METHYLHEXANE	-	7	-	-	-	-
43230	3-METHYL PENTANE	-	6	-	-	-	-
43223	3-METHYL-1-BUTENE	1	3	-	-	-	-
43211	3-METHYL-1-PENTENE	1	4	-	-	-	-
43270	3-METHYL-T-2-PENTENE	-	4	-	2	-	-
43298	3-METHYLHEPTANE	-	8	-	-	-	-
43295	3-METHYLHEXANE	-	7	-	-	-	-
43293	4-METHYL-T-2-PENTENE	-	4	-	2	-	-
43297	4-METHYLHEPTANE	-	8	-	-	-	-
45221	A-METHYLSTYRENE	-	2	1	1	-	-
50025	A-PINENE	1	8	-	-	-	-
43503	ACETALDEHYDE	-	1	-	1	-	-
43404	ACETIC ACID	-	1	-	-	-	1

TABLE B-2. (Continued)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43551	ACETONE	-	3	-	-	-	-
43702	ACETONITRILE	-	1	-	-	-	1
43206	ACETYLENE	-	1	-	-	-	1
43704	ACRYLONITRILE	1	1	-	-	-	-
50015	ANTHRACENE	-	8	1	-	-	-
50020	B-METHYLSTYRENE	1	-	1	1	-	-
50026	B-PINENE	1	8	-	-	-	-
45201	BENZENE	-	1	-	-	-	5
50024	BENZYLCHLORIDE	-	1	1	-	-	-
43213	BUTENE	1	2	-	-	-	-
43510	BUTYRALDEHYDE	-	3	-	1	-	-
50003	C-3-HEXENE	1	4	-	-	-	-
43115	C-7 CYCLOPARAFFINS	-	7	-	-	-	-
43116	C-8 CYCLOPARAFFINS	-	8	-	-	-	-
43117	C-9 CYCLOPARAFFINS	-	9	-	-	-	-
43511	C3 ALDEHYDE	-	2	-	1	-	-
43512	C5 ALDEHYDE	-	4	-	1	-	-
43289	C6 OLEFINS	1	4	-	-	-	-
43294	C7-OLEFINS	1	5	-	-	-	-
43513	C8 ALDEHYDE	-	7	-	1	-	-
43290	C8 OLEFINS	1	6	-	-	-	-
43807	CARBON TETRABROMIDE	-	-	-	-	-	1
43804	CARBON TETRACHLORIDE	-	-	-	-	-	1
43443	CELLOSOLVE® ACETATE	-	4	-	2	-	-
43803	CHLOROFORM	-	-	-	-	-	1
43217	CIS-2-BUTENE	-	2	-	2	-	-
43227	CIS-2-PENTENE	-	3	-	2	-	-
50019	CRYOFLOURANE (FREON 114)	-	-	-	-	-	2
43248	CYCLOHEXANE	-	6	-	-	-	-
43264	CYCLOHEXANONE	-	5	-	1	-	-
43273	CYCLOHEXENE	1	4	-	-	-	-
43242	CYCLOPENTANE	-	5	-	-	-	-
43292	CYCLOPENTENE	1	3	-	-	-	-
43207	CYCLOPROPANE	-	3	-	-	-	-
50027	D-LIMONENE	1	6	-	2	-	-
43320	DIACETONE ALCOHOL	-	5	-	1	-	-
43823	DICHLORODIFLUOROMETHANE	-	-	-	-	-	1
43802	DICHLOROMETHANE	-	-	-	-	-	1
50018	DIMETHYL ETHER	-	2	-	-	-	-
43450	DIMETHYL FORMAMIDE	-	-	-	-	-	3
50017	DIMETHYL-2,3,DIHYDRO-1H-INDENE	-	5	1	-	-	-
45103	DIMETHYLETHYLBENZENE	-	4	1	-	-	-
50012	DIMETHYLNAPHTHALENE	-	6	1	-	-	-
43287	DOCOSANE	-	22	-	-	-	-
43285	EICOSANE	-	20	-	-	-	-

TABLE B-2. (Continued)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43202	ETHANE	-	.4	-	-	-	1.6
43433	ETHYL ACETATE	-	3	-	-	-	1
43438	ETHYL ACRYLATE	-	3	-	2	-	-
43302	ETHYL ALCOHOL	-	2	-	-	-	-
43812	ETHYL CHLORIDE	-	-	-	-	-	2
43351	ETHYL ETHER	-	3	-	1	-	-
43219	ETHYLACETYLENE	-	4	-	-	-	-
43721	ETHYLAMINE	-	1	-	-	-	1
45203	ETHYLBENZENE	-	2	1	-	-	-
43288	ETHYLCYCLOHEXANE	-	8	-	-	-	-
43203	ETHYLENE	-	-	-	-	1	-
43815	ETHYLENE DICHLORIDE	-	-	-	-	1	-
43370	ETHYLENE GLYCOL	-	2	-	-	-	-
43601	ETHYLENE OXIDE	-	1	-	-	-	1
50011	ETHYLNAPHTHALENE	-	6	1	-	-	-
43502	FORMALDEHYDE	-	-	-	1	-	-
43368	GLYCOL	-	1	-	1	-	-
43367	GLYCOL ETHER	-	1	-	1	-	-
43286	HENEICOSANE	-	21	-	-	-	-
43282	HEPTADECANE	-	17	-	-	-	-
43232	HEPTANE	-	7	-	-	-	-
50005	HEPTENE	1	5	-	-	-	-
43281	HEXADECANE	-	16	-	-	-	-
43231	HEXANE	-	6	-	-	-	-
43214	ISO-BUTANE	-	4	-	-	-	-
43306	ISO-BUTYL ALCOHOL	-	4	-	-	-	-
43304	ISO-PROPYL ALCOHOL	-	3	-	-	-	-
43446	ISOBUTYL ACETATE	-	6	-	-	-	-
43451	ISOBUTYL ISOBUTYRATE	-	7	-	1	-	-
43215	ISOBUTYLENE	-	3	-	1	-	-
43120	ISOMERS OF BUTENE	-	2	-	2	-	-
45105	ISOMERS OF BUTYLBENZENE	-	4	1	-	-	-
43109	ISOMERS OF DECANE	-	10	-	-	-	-
45106	ISOMERS OF DIETHYLBENZENE	-	4	1	-	-	-
43112	ISOMERS OF DODECANE	-	12	-	-	-	-
45104	ISOMERS OF ETHYLTOLUENE	-	3	1	-	-	-
43106	ISOMERS OF HEPTANE	-	7	-	-	-	-
43105	ISOMERS OF HEXANE	-	6	-	-	-	-
45234	ISOMERS OF METHYLPROP. BENZENE	-	4	1	-	-	-
43108	ISOMERS OF NONANE	-	9	-	-	-	-
43107	ISOMERS OF OCTANE	-	8	-	-	-	-
43114	ISOMERS OF PENTADECANE	-	15	-	-	-	-
43122	ISOMERS OF PENTANE	-	5	-	-	-	-
43121	ISOMERS OF PENTENE	-	3	-	2	-	-
45108	ISOMERS OF PROPYLBENZENE	-	3	1	-	-	-

TABLE B-2. (Continued)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43113	ISOMERS OF TETRADECANE	-	14	-	-	-	-
43111	ISOMERS OF TRIDECANE	-	13	-	-	-	-
45107	ISOMERS OF TRIMETHYLBENZENE	-	3	1	-	-	-
43110	ISOMERS OF UNDECANE	-	11	-	-	-	-
45102	ISOMERS OF XYLENE	-	2	1	-	-	-
43243	ISOPRENE	1	1	-	2	-	-
43444	ISOPROPYL ACETATE	-	5	-	-	-	-
43119	LACTOL SPIRITS	-	8	-	-	-	-
50022	M-CRESOL (3-METHYLBENZENOL)	-	-	1	1	-	-
45212	M-ETHYLTOLUENE	-	3	1	-	-	-
45205	M-XYLENE	-	2	1	-	-	-
43201	METHANE	-	-	-	-	-	1
43432	METHYL ACETATE	-	-	-	-	-	3
43301	METHYL ALCOHOL	-	1	-	-	-	-
43445	METHYL AMYL ACETATE	-	8	-	-	-	-
43801	METHYL CHLORIDE	-	-	-	-	-	1
43552	METHYL ETHYL KETONE	-	3	-	1	-	-
43560	METHYL ISOBUTYL KETONE	-	5	-	1	-	-
43559	METHYL N-BUTYL KETONE	-	5	-	1	-	-
43209	METHYLACETYLENE	-	1.5	-	-	-	1.5
50016	METHYLANTHRACENE	-	9	1	-	-	-
43261	METHYLCYCLOHEXANE	-	7	-	-	-	-
43262	METHYLCYCLOPENTANE	-	6	-	-	-	-
43272	METHYLCYCLOPENTENE	1	4	-	-	-	-
43819	METHYLENE BROMIDE	-	-	-	-	-	1
50010	METHYLNAPHTHALENE	-	5	1	-	-	-
43118	MINERAL SPIRITS	-	7	-	1	-	-
45801	MONOCHLOROBENZENE	-	5	-	-	-	1
43212	N-BUTANE	-	4	-	-	-	-
43435	N-BUTYL ACETATE	-	5	-	-	-	1
43305	N-BUTYL ALCOHOL	-	4	-	-	-	-
43238	N-DECANE	-	10	-	-	-	-
43255	N-DODECANE	-	12	-	-	-	-
43260	N-PENTADECANE	-	15	-	-	-	-
43220	N-PENTANE	-	5	-	-	-	-
43303	N-PROPYL ALCOHOL	-	3	-	-	-	-
45209	N-PROPYLBENZENE	-	3	1	-	-	-
43259	N-TETRADECANE	-	14	-	-	-	-
43258	N-TRIDECANE	-	13	-	-	-	-
45101	NAPHTHA	-	8	-	-	-	-
43284	NONADECANE	-	19	-	-	-	-
43235	NONANE	-	9	-	-	-	-
50021	O-CRESOL (2-METHYLBENZENOL)	-	-	1	1	-	-
45211	O-ETHYLTOLUENE	-	3	1	-	-	-
45204	O-XYLENE	-	2	1	-	-	-

TABLE B-2. (Concluded)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43283	OCTADECANE	-	18	-	-	-	-
43233	OCTANE	-	8	-	-	-	-
43265	OCTENE	1	6	-	-	-	-
50023	P-CRESOL (4-METHYLBENZENOL)	-	-	1	1	-	-
45206	P-XYLENE	-	2	1	-	-	-
43817	PERCHLOROETHYLENE	-	-	-	-	-	2
45300	PHENOLS	-	-	-	-	-	6
50006	PROPADIENE	-	1	-	2	-	-
43204	PROPANE	-	1.5	-	-	-	1.5
43504	PROPRIONALDEHYDE	-	2	-	1	-	-
43434	PROPYL ACETATE	-	4	-	-	-	1
43205	PROPYLENE	1	1	-	-	-	-
43369	PROPYLENE GLYCOL	-	2	-	1	-	-
43602	PROPYLENE OXIDE	-	2	-	-	-	1
50013	PROPYLNAPHTHALENE	-	7	1	-	-	-
43208	PROPYNE	-	2	-	-	-	1
45216	SEC-BUTYLBENZENE	-	4	1	-	-	-
45220	STYRENE	-	1	1	1	-	-
43123	TERPENES	1	8	-	-	-	-
43309	TERT-BUTYL ALCOHOL	-	-	-	-	-	4
45215	TERT-BUTYLBENZENE	-	4	1	-	-	-
43390	TETRAHYDROFURAN	-	3	-	1	-	-
45232	TETRAMETHYLBENZENE	-	4	1	-	-	-
45202	TOLUENE	-	1	1	-	-	-
43216	TRANS-2-BUTENE	-	2	-	2	-	-
43226	TRANS-2-PENTENE	-	3	-	2	-	-
45233	TRI/TETRAALKYL BENZENE	-	5	1	-	-	-
43824	TRICHLOROETHYLENE	-	-	-	-	1	-
43811	TRICHLOROFLOUROMETHANE	-	-	-	-	-	1
43821	TRICHLOROTRIFLOUROETHANE	-	-	-	-	-	2
43740	TRIMETHYL AMINE	-	3	-	-	-	-
43822	TRIMETHYLFLUOROSILANE	-	-	-	-	-	3
50014	TRIMETHYLNAPHTHALENE	-	7	1	-	-	-
43241	UNDECANE	-	11	-	-	-	-
43000	UNKNOWN SPECIES	.1	4	.25	.32	.16	-
43860	VINYL CHLORIDE	-	-	-	-	1	-
45401	XYLENE BASE ACIDS	-	2	1	-	-	-

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